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Application of a GaPO₄ Crystal Microbalance for the Detection of Coke Formation in High-Temperature Reactors and Solid Oxide Fuel Cells

Jason Millichamp,[†] Ebrahim Ali,[†] Nigel P. Brandon,[†] Richard J. C. Brown,[§] David Hodgson,[†] Christos Kalyvas,[‡] George Manos,[†] and Daniel J. L. Brett^{*,†}

[†]Centre for CO₂ Technology, Department of Chemical Engineering, University College London, London, WC1E 7JE, U.K.

[‡]The Energy Futures Lab, Imperial College London, SW7 2AZ, U.K.

[§]The National Physical Laboratory, Teddington, TW11 0LW, U.K.

[‡]Department of Chemistry, Imperial College London, SW7 2AZ, U.K.

ABSTRACT: Piezoelectric crystal microbalance devices based on gallium orthophosphate (GaPO₄) have recently become commercially available. This material allows for operation at over 900 °C and therefore has potential as an analytical technique for the study of surface reactions at high temperatures. This paper describes preliminary work to assess the suitability of this technology for such applications. Change in oscillation frequency associated with temperature and gaseous environment is studied, and the ability to detect coke formation on a Ni-modified crystal is demonstrated. These results suggest that the technology can be developed as a low cost, high sensitivity gravimetric sensor for monitoring surface processes in high temperature chemical reactors such as reformers and solid oxide fuel cells (SOFCs)

1. INTRODUCTION

The quartz crystal microbalance (QCM) is a mass sensing device with the ability to measure very small mass changes (in the range of ng cm⁻²) in real time, occurring at the electrodes bonded to piezoelectric quartz crystals. The operating principle of the QCM relies upon the piezoelectric effect exhibited by suitably cut quartz, first discovered by Pierre and Marie Curie in 1880;¹ while its quantitative basis was established by Sauerbrey² who first showed that the shift in resonant frequency of a QCM can be correlated to the mass deposited upon it.

The QCM has been extensively used in applications ranging from gas phase detection, metal deposition sensing, and analytical electrochemistry to biosensors and drug design and analysis. In most of these applications, experiments are performed at or near room temperature (up to 50 °C). The commonly used AT-cut quartz (SiO₂) crystals have a minimal frequency dependence on temperature at low temperatures, up to 150 °C. However, at elevated temperatures, the effect of temperature causes very large resonator instability and thus affects the accuracy of mass measurements. In addition, the QCM can only be used up to the Curie temperature (~573 °C), above which the crystallographic structure changes and the quartz loses its piezoelectric properties.³ The process is irreversible and the structure that supports piezoelectric behavior does not return when the temperature is brought back below the Curie temperature. The crystal is thus irreversibly damaged once the Curie temperature is reached.

Gallium orthophosphate (GaPO₄) is a piezoelectric material offering greater high-temperature stability than conventional AT-cut quartz crystals.⁴ The temperature coefficient for quartz increases with the cube of the sensor temperature from -25 Hz °C⁻¹ at 30 °C to 650 Hz °C⁻¹ at 393 °C.⁵ In contrast, the temperature coefficient of the GaPO₄ (Y-11.1°) crystal decreases linearly with temperature, reaching 3 Hz °C⁻¹ at 450 °C.⁵ Further advantages of GaPO₄ over the quartz crystal include a

higher electromechanical coupling coefficient (the constant that quantifies the electric to acoustic energy conversion efficiency) and lower damping (any effect inherent to a system that tends to reduce the amplitude of oscillations).⁴ These properties render GaPO₄ a strong candidate for resonator applications at high temperatures.

The high temperature performance of GaPO₄ has been demonstrated in a number of studies. GaPO₄ crystals have been successfully used for *in situ* measurements of Al₂O₃ and TiO₂ film growth by atomic layer deposition at 450 °C.⁵ Studies have also shown the possibility for gravimetric analysis using GaPO₄ resonators up to temperatures of 720 °C.⁶ Evidence exists to suggest that operation above 750 °C will lead to a significant reduction in quality factor and material degradation over time.⁷

Our research in this area is focused on exploiting the properties of the GaPO₄ crystal microbalance (GCM) for use as an *in situ* sensor for the study of high temperature heterogeneous catalytic processes. For example, the use as an analytical tool for the study of carbon deposition on solid oxide fuel cell (SOFC) anodes or reformer catalysts during operation on hydrocarbon fuel.⁸

In this paper we demonstrate the use of the GCM at high temperatures, examining the bounds of practical use; operation in reducing and oxidizing environments (partial pressure of oxygen; *p*O₂ dependence) and examining how carbon deposition on a nickel surface can be detected when the sensor is exposed to a methane environment representative of a low steam-to-carbon fuel, as found at the anode compartment of an SOFC.

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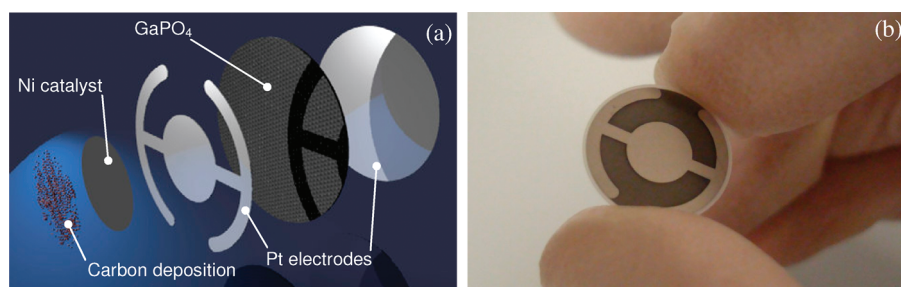


Figure 1. (a) Exploded view of showing the layers of the device; (b) photo of GCM showing “double anchor” metallization.

2. EXPERIMENTAL SECTION

The GCM devices used in this study were based on gallium orthophosphate crystals (Y-11.1° cut, R-30, Q-factor = 70000, resonant frequency = 5.8 ± 0.1 MHz, sensitivity $\approx 0.3 \text{ ng Hz}^{-1}$) with a double anchor metallization (curvature = 2 dioptre) on one side and full metallization (flat) on the other. On both sides the electrode is platinum ($\sim 200 \text{ nm}$) with a titanium adhesion underlayer ($\sim 20 \text{ nm}$). These devices are commercially available from Piezocryst Advanced Sensorics GmbH (Graz, Austria). Figure 1 shows an exploded view illustrating each of the layers, along with a photo of the device.

The crystals were mounted in a holder constructed from pyrophyllite machinable ceramic and electrical contact was made using coiled platinum wire (0.25 mm diameter 99.99+% purity, Goodfellow, UK). The crystal holder was positioned within a sealed quartz tube in a horizontal split tube furnace in order to control the temperature and gaseous environment of the GCM. The oscillation frequency of the GCM was measured using a Q-pod Quartz Crystal Monitor (Inficon, UK) which interfaces to a PC. The gas environment was controlled using calibrated mass flow controllers (EL-FLOW, Bronkhorst, UK).

For the $p\text{O}_2$ and methane exposure experiments, samples were heated to 600°C in a particular environment (H_2 for the CH_4 tests) with a flow rate of $100 \text{ cm}^3 \text{ min}^{-1}$ and held for approximately 2 h to equilibrate. Once steady state was achieved, the requisite gaseous environment was introduced.

For the carbon deposition study, Ni was electrodeposited onto the Pt electrodes using a Watts bath consisting of a solution of 0.647 M H_3BO_3 , 0.285 M $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, and 0.047 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$.^{9,10} Nitrogen was bubbled through the solution to rid the chamber of oxygen as well as being used during the plating experiments to rid the sample surface of H_2 bubbles formed. Nickel was used as the counter electrode together with a $\text{Hg}/\text{Hg}_2\text{Cl}_2$ (SCE) reference electrode. An Autolab PGSTAT-302N (Metrohm Autolab, Netherlands) potentiostat, was used to perform Ni plating at -1.1 V versus SCE for 900 s. The measured mass change associated with the electrodeposited Ni layer corresponds to a thickness of $\sim 3 \mu\text{m}$; SEM and EDS analysis (not shown) confirmed a full and even nickel coating of Ni on Pt.

3. RESULTS AND DISCUSSION

To assess the suitability of the GCM as a sensor for monitoring surface processes in high temperature reactors, the effect of temperature and $p\text{O}_2$ on the oscillation of the crystal device was studied, together with the effect of coke formation on the surface when exposed to a methane feed.

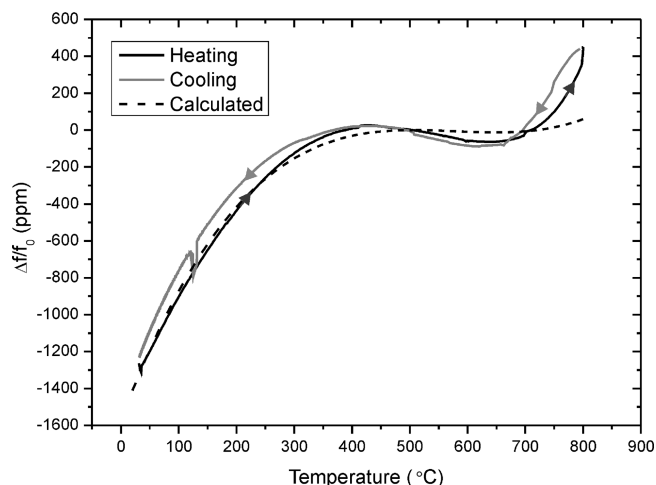


Figure 2. Graph showing the effect of temperature on the oscillation frequency of the GCM based on experiment and calculation using the manufacturer's empirical expression. Temperature scan rate is 5°C min^{-1} , and operation is in air.

3.1. Effect of Temperature on Crystal Oscillation Frequency. For the GCM to act as a reliable and practical sensor, the effect of temperature on its performance must be determined such that it can be controlled or compensated for in order to achieve robust measurements.

At room temperature, the sensor displays a $\pm 0.42 \text{ Hz}$ frequency scatter when data was collected at 10 scans per second. This corresponds to a mass sensing level of $\sim 0.0110 \mu\text{g}$ on a reported instrument resolution of 0.05 Hz at 6 MHz. Extended testing over 5 h showed a 31 Hz shift in frequency, but was related to a 0.7°C change in temperature of the GCM over this period; which, when corrected for temperature showed a drift of only -0.74 Hz , corresponding to a mass change of $0.02 \mu\text{g}$.

Figure 2 shows the variation in oscillation frequency as a function of temperature. The furnace temperature was increased from room temperature at a rate of 5°C min^{-1} , and a thermocouple was placed close to the GCM holder to measure the local temperature of the device.

GCM crystals are calibrated to 505°C by the manufacturer due to their angle of cut, Y-11.1°, therefore it is usual to calculate or present the change in frequency relative to this point. This allows for better comparison between individual crystals that would each have a slightly different starting frequency. Thus the y-axis displays change in frequency as $\Delta f/f_0$ in parts per million (ppm). Here, f_0 (the actual fundamental frequency) is taken as the frequency at 505°C or f_{505} , creating $\Delta f/f_{505}$.

Along with the experimental data, Figure 2 shows the frequency variation predicted by the empirically derived expression provided by the crystal manufacturer (Piezocryst Advanced Sensorics):

$$f_s(T) = f_s(T_0)[1 + a(T - T_0) + b(T - T_0)^2 + c(T - T_0)^3]$$

where T_0 is the temperature constant at the zero point of 505 °C; T is temperature (°C); a , b , and c are constants, $a = 0.00831 \text{ ppm } ^\circ\text{C}^{-1}$, $b = -0.00186 \text{ ppm } ^\circ\text{C}^{-2}$, $c = 8.5 \times 10^{-6} \text{ ppm } ^\circ\text{C}^{-3}$; and $f_s(T_0)$ is the frequency as a function of temperature at the zero point (dependent on individual crystals).

The experiments showed that the difference between the heating and cooling scan is exacerbated by an increase in the rate of temperature change. Therefore, this is not considered to be an inherent hysteresis affect associated with the material/device, but rather a temperature lag effect. The difference between the experimental results and the predicted performance may be a consequence of heating rate, manufacture variance between crystals and/or the effect of the holder used for the GCM.

The angle of cut determines the crystal's characteristics, such as coupling, dampening, and inversion temperature. In the case of the Y-11.1° cut, the flattest temperature dependent frequency shift is at 505 °C and remains relatively flat up to 700 °C. Such a crystal would be particularly suitable for studying intermediate temperature (IT) SOFCs¹¹ which operate in this temperature range.

Stable operation has been monitored up to 900 °C over short periods; however, attempts to sinter catalyst material onto the electrode at temperatures over 1350 °C resulted in irreversible loss of oscillator performance.

3.2. Effect of $p\text{O}_2$ on Sensor Performance. Temperature is not the only operational condition that can affect the response of the GCM; changes in the chemical environment may affect the materials of the device, leading to unaccountable frequency change and potentially to failure. For example, the $p\text{O}_2$ is known to have an effect on piezoelectric materials such as langasite.¹² Delamination during these processes was dismissed as the unaccountable shift due to the crystals returning to their original frequency. Changes in $p\text{O}_2$ during operation may result in oxidation or reduction of the crystal or electrode material, thus affecting the piezoelectric properties or the mass of the electrode. In the operating environment of an SOFC, the $p\text{O}_2$ can vary over a large range (between that for pure air and H_2), and can have a significant impact on the properties of the electrolyte and electrode materials.

Studies have shown that GaPO_4 holds one of the lowest electrical conductivities of any piezoelectric material, and hence is minimally affected by the altering relationship between oxygen vacancies and electrical conductivity during oxidation/reduction changes.¹³ However, more work needs to be done to assess the affect of operating environments relevant to practical applications of this sensor technology.

The GaPO_4 itself is not the only part of the device potentially affected by a change in $p\text{O}_2$. The Pt electrodes used may also undergo oxidation and reduction at the surface. This is not expected to be an issue at IT-SOFC relevant temperatures since platinum oxides decompose at lower temperatures leaving pure Pt (PtO at 325 °C and PtO_3 at 450 °C).¹⁴ However, the titanium underlayer used to bond the platinum to the GaPO_4 may be an issue. Ti forms stable oxides at operational temperatures¹⁵ and it has been found that oxygen can diffuse through Pt to form TiO_2 .

Titanium can also diffuse through Pt at temperatures around 600 °C.¹⁵ As a result, oxide precipitates can form at grain boundaries within the Pt, this affects the adhesion of the Pt layer and the frequency response of the device.¹⁵

Testing the crystals in varying gas environments has demonstrated shifts in frequency over time when held at constant temperature. Figure 3 shows three tests carried out on the same crystal for different gas composition transitions. For each test, the initial gas environment was exposed to the sensor from room temperature to 600 °C. Note that nitrogen is always used to purge the system before changing between H_2 and air. In each case, the frequency shift is normalized to zero at the start of the run.

When switching between gas feeds, changes in the physical properties of the fluids can lead to slight changes in the temperature of the sensor due to differences in the thermal properties of the different fluids; however, frequency changes caused by these small transient temperature shifts are not significant compared to the frequency changes induced by the change in chemical nature of the gas.

Transition from any environment to an inert N_2 environment does not result in significant frequency change. Likewise, transition from N_2 back to the previous gas showed no change. This is consistent with frequency transitions being the consequence of the change in $p\text{O}_2$ (oxidizing/reducing potential) of the gas. In Figure 3a it can be seen that transition to reducing environment (H_2) from a previously oxidizing environment (air) results in a frequency increase (effective mass decrease). Transition the other way, Figure 3c, shows that the opposite is observed. Over the time period of the experiments, fully reversible frequency response was not observed; however, this may be a consequence of the oxidation process being a slower reaction and not fully captured.

Although no supporting information is available as to the surface state of the Pt, the frequency changes observed are consistent with the growth and removal of oxide on the Pt electrode surface. Taking the frequency transition in hydrogen for a crystal previously exposed to air (Figure 3a), the change corresponds to a mass change of 50 μg which is consistent with a platinum oxide layer of $\sim 25 \text{ nm}$. However, as stated above, the Ti underlayer may also play a role in this frequency change. In addition, the temperature at which the experiments were performed (600 °C) Pt oxides are not expected to be stable on the surface.

The response observed for these transitions was highly reproducible. Common features observed between runs on different crystals include the three-part profile observed in the H_2 exposure region in Figure 3a. This is composed of an initial increase in frequency, followed by an approximately linear period and finally a more rapid transition and relaxation to a constant stable frequency. The cause of this is uncertain; the fact that there is a period over which one gas environment displaces another (at the flow rates used, it takes ca. 1700 s for the new gas to fill the reactor and displace the previous gas) will affect the transition profile and make the absolute kinetics of the process difficult to determine. In the case of the transition to air in Figure 3c, an initial increase in frequency is consistently observed, sometimes by as much as 25 ppm, which is also unexplained at present.

3.3. Detection of Coke Formation. In SOFCs, carbon formation occurs when a carbonaceous fuel with an insufficient steam-to-carbon ratio is exposed to the metallic component of the anode such as nickel. This deposit blocks reaction sites, which

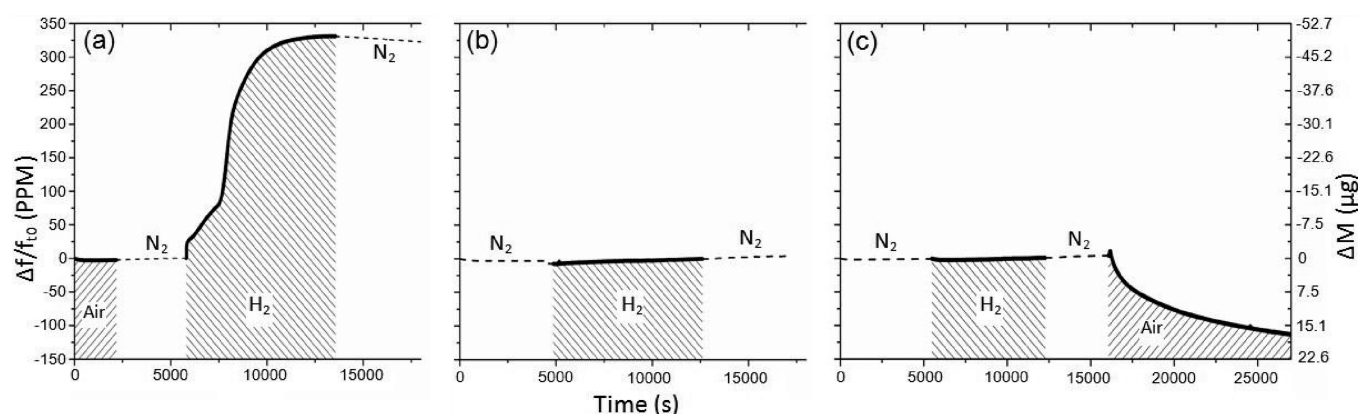


Figure 3. Frequency and mass shift vs time plots showing the effect of transition between different gaseous environments for the GCM sensor at 600 °C: (a) transition to a reducing environment following exposure to air; (b) transition to a reducing environment following exposure to a reducing atmosphere; and (c) transition to air following exposure to a reducing atmosphere. Note that the frequency and mass scales apply to all sections.

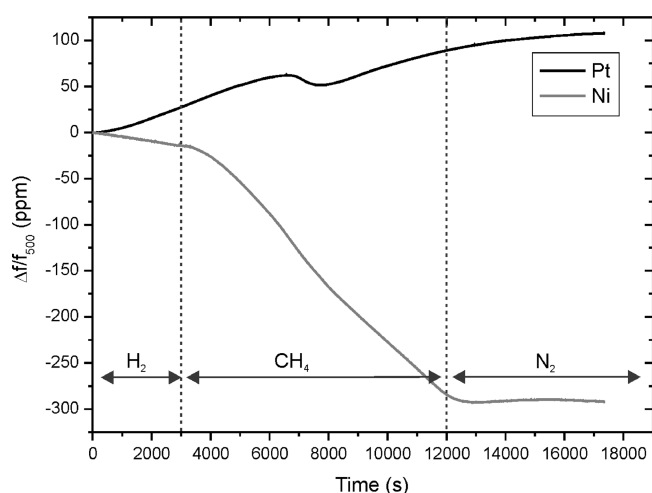


Figure 4. GCM frequency change in transition between $\text{H}_2/\text{CH}_4/\text{N}_2$ at 600 °C for Ni and Pt electrodes.

results in a less accessible triple phase boundary¹⁶ and therefore performance degradation. This is a major durability issue for SOFCs and the subject of intense study and efforts to mitigate it. In developing the GCM for high temperature sensor applications, coke formation on SOFC anode-mimetic layers is the first priority of this work. Although other chemicals and fuels have a greater propensity for coke formation (ethylene and many aromatic compounds for example), methane is the most common hydrocarbon fuel used in SOFCs and used here to see if the GCM can detect coke formation.

The bare Pt GCM was first exposed to a pure stream of methane at 600 °C following operation in hydrogen, as shown in Figure 4. The introduction of methane had relatively little effect on the frequency response of the GCM, a slight decrease in frequency superimposed on a positively drifting baseline response may be a consequence of carbon formation.

To make the GCM electrodes more representative of an SOFC anode, a layer of Ni was electrodeposited on to the Pt electrode. Figure 4 shows that introduction of CH_4 to the chamber resulted in a monotonic decrease in frequency (increase in mass) that abated when the gas supply was switched to N_2 . According to the Sauerbrey equation, the total mass change over 8690 s

corresponded to 41 μg or 91 nm thickness, assuming a solid even layer of carbon formed on the surface of the electrode.

4. CONCLUSIONS

Microbalance technology based on GaPO_4 crystals has shown to be effective for high temperature operation. The results show the variation of oscillation with temperature, with stable operation at temperatures in excess of 900 °C.

Transition between air and H_2 environments showed a frequency change consistent with the oxidation and reduction of the surface, which may be a result of the Pt or Ti underlayer.

When exposed to pure methane, mass increase associated with coke formation on the surface of Ni is observed (but not with the Pt electrode). This result suggests that the GCM has promise as a highly sensitive, low cost sensor for the study of heterogeneous catalytic process at high temperatures, as well as a practical in situ device for incorporation into reactors for control and monitoring purposes.

The example given here is for a Ni layer directly deposited onto the crystal; it is appreciated that most heterogeneous processes use supported catalysts rather than metal films. Future work will examine the potential to co-deposit catalyst and support, the challenge here being not to overload the crystal and lose oscillation and to understand how the frequency response for a nonhomogeneous surface will respond to mass deposition.

In addition, to take this technology forward, it will be necessary to develop a reliable sensor housing/holder; understand the factors that contribute to frequency drift at high temperatures and minimize this effect; incorporate temperature control or compensation; investigate surface layers; and modification that allows relevant materials and interactions to be investigated.

The assumptions are implicit in the use of the Sauerbrey equation for the deposited layers of interest. To incorporate the sensor into a practical control system, operational protocols will need to be established. These include calibration, drift and temperature compensation, and surface regeneration. For example, it has been shown that very high steam ratios can allow for the cleaning of anodes.¹⁷

Future work will also investigate the use of alternative underlayers and obtain in situ information about the state of the Pt or

Ni surface during operation by using Raman spectroscopy, as previously demonstrated for SOFC anodes.¹⁸

AUTHOR INFORMATION

Corresponding Author

*E-mail: d.brett@ucl.ac.uk.

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