Available online at www.sciencedirect.com

ScienceDirect

IFAC-PapersOnLine 48-1 (2015) 041–046

Mathematical Modelling of molecular adsorption in zeolite coated frequency domain sensors

Fabian N. Murrieta-Rico[a], **Paolo Mercorelli**[b], **Oleg Yu. Sergiyenko**[c], **Vitalii Petranovskii**[ad], **Daniel Hernandez-Balbuena**[c] and **Vera Tyrsa**[c]

[a]*Universidad Nacional Autónoma de México, Ensenada, BC 22860 Mexico*
(e-mails: fmurriet@cicese.edu.mx; vitalii@cnyn.unam.mx)
[b]*Leuphana University of Lueneburg, Lueneburg, Germany*
(e-mail: mercorelli@uni.leuphana.de)
[c]*Universidad Autónoma de Baja California, 21280 Mexicali, México*
(e-mails: srgnk@uabc.edu.mx; dhernan@uabc.edu.mx; vera-tyrsa@mail.ru)
[d]*On the sabbatical leave at: Departamento de Investigación en Zeolitas*
Instituto de Ciencias BUAP, Puebla 72570, México

Abstract: Fast and accurate information is important for most monitoring, data acquisition, and monitoring systems; sensors are transducers that allow to accomplish such task. In this work different kinds of resonant sensors known as frequency domain sensors are reviewed; also frequency measurement techniques are explored; finally resolution improvement is proposed and analyzed for using frequency domain sensors by mathematical modelling.

Keywords: sensors modeling, zeolite, FDS, microcantilever, frequency measurement, relative error.

1. INTRODUCTION

Sensors are used to get information from the environment for monitoring and control where accurate and fast information is required. In such systems, the response and data processing time is critical. A sensor is a transducer that transforms a measurand quantity into an electrical measurement value, usually voltage, current or frequency (Benes et al., 1995).

Highly sensitive sensors can be used for detecting chemical compounds and measuring their concentration. Such devices are of interest in a wide range of areas like such as healthcare, hazardous compounds detection, national security, aerospace and automotive industries. Some of this sensors are made of a self-resonant component (f.i. piezoelectric materials), and are coated with a layer of a material that in some way reacts to the target compound to be detected. Zeolites are materials used for sensitive layer in sensors used for chemical compound detection.

In these sensors the resonant frequency of the sensor shifts according to the interaction resulting of the analyte and the detection layer. For proper use of these sensors fast and accurate frequency meters are needed, most of the frequency meters require long times for measuring. In this work, a method for improving resolution in sensors used for chemical compounds detection is proposed, and particular cases are analyzed by mathematical modelling.

2. ZEOLITES

Zeolites are crystalline, hydrated aluminosilicates having microporous, regular structures. The zeolite micropores are of molecular size (diameters could be as small as 2 nm), which give them adsorption, catalytic, and ion-exchange properties of paramount importance in the chemical industrial field. Zeolites can either be the essential components of chemical sensors or be used to increase their selectivity and sensitivity, as a functional element, with ion-conducting, adsorption of selective molecules. Over 200 zeolites frameworks with different topologies have been reported ("International Zeolite Association,"). Examples of zeolites frameworks used on chemical compounds detection are shown on Fig. 1.

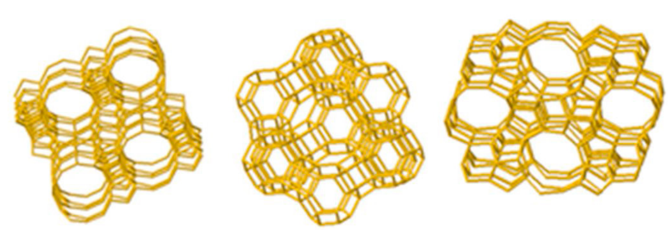

Fig. 1. Zeolite framework topologies used on chemical compounds detection: a) BEA used for sensing pentane and hexane (Mintova and Bein, 2001), b) FAU for detecting SO2 (Osada et al., 1998), c) MFI for detection of ethanol (Vilaseca et al., 2003).

The zeolite-based devices fabrication techniques can be separated into three main groups: i)direct synthesis of zeolite crystals on a support, ii) seed methods, and iii) attachment of crystals on functionalized surfaces (Mintova and Bein, 2001).

Zeolites frameworks are constructed by crystalline silica (SiO_2), in some places it is replaced the Si^{4+} by Al^{3+}, this gives a negative charge to the framework (Al_2O_3). Upon adsorption, mass changes as well as optical properties are altered, which have been used for the sensor transduction. Although there are several zeolite properties used for sensing,

Peer review under responsibility of International Federation of Automatic Control.
10.1016/j.ifacol.2015.05.060

in this work we focus in the mass change that occurs during the adsorption process in the coating with a zeolite film on a sensor. Now the point is how to detect this proportional mass change, and convert it into proportional electrical signal which is more natural for further processing by computer. The next section is dedicated to solve this problem.

3. QUARTZ CRYSTAL MICROBALANCES (QCM)

A QCM is an ultra-sensitive weighing device that utilizes the mechanical resonance of piezoelectric single crystalline quartz (Saraoğlu and Kırankabeş, 2009). A QCM works

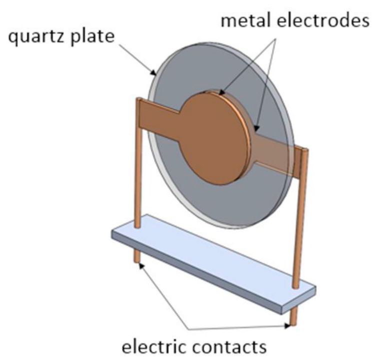

Fig. 2. In a QCM when the quartz crystal plate experiments a change on the pressure applied on its quartz plate, a frequency shift in the QCM is generated.

under the piezoelectric effect, where a piezoelectric element has a change on its electrical response when it is exposed to a change on the pressure applied on its surface (Fig. 2).

A material that adsorbs chemical compounds changes its mass when adsorbs molecules of the target analyte, if a QCM is coated with such material (a sensitive layer), a stress is generated on the crystal's surface. The typical frequency response of QCM devices is from KHz to a few MHz. In Table 1 a summary of QCM coated with zeolites and their applications.

Table 1. QCM coated with zeolites

Chemical compound detected	Zeolite used for coating	Natural resonance Frequency	Maximum Frequency Shift
Acetone	AG^+ZSM-5	8 MHz	400 Hz
SO_2	Faujasite	5.4 MHz	130 Hz

7. IMPROVING RESOLUTION IN FREQUENCY MEASUREMENT PROCESS

The objectives of digital measurements for frequency time parameters in a signal, are to increase accuracy, speed and metrological reliability of measurement of absolute and relative values; also it is desirable to expand functionality, measuring range, possibilities of measuring instruments and automatize completely all procedures of measurement, control, digital processing, parametric adaptation and self-testing, to reduce circuitry, cost, weight, dimensions and power consumption.

State of the art frequency measurement techniques require high processing times and high computational power, this means that in order to get better accuracy they need more time for calculations, that's why their implementation is not suitable for embedded systems (Kia et al., 2007). The frequency measurement principle of rational approximation was proposed by Sergiyenko-Hernandez (Hernández Balbuena et al., 2009), applications for the FDS in the industries also have been proposed based on this method (Molina, 2013; Murrieta R et al., 2010; Sergiyenko et al., 2012), and it has shown important advantages over other frequency measurement techniques (Johansson, 2005). Among these improvements are invariance to timing jitter and the fact that uncertainty of the measurement does not depend on the time of measurement.

Before to be able to measure the frequency, the signal source needs to go through a signal conditioning process, where the raw signal is changed to a more convenient form while the

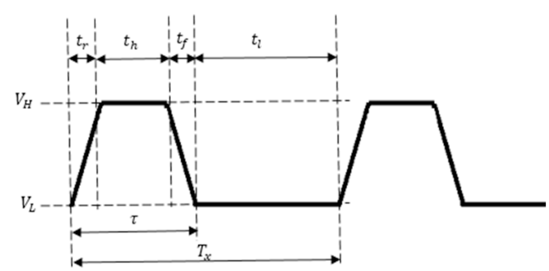

Fig. 3. Signal after conditioning process: time relationships.

original frequency is maintained (Murrieta-Rico et al., 2014). In this conditioned signal the time of the pulse width (τ) is less than the 50% of the unknown period time (T_x); this means that the relationship $\tau < t_l$ holds, where t_l is the lower level time. The characteristics of the conditioned signal are shown on Fig. 3.Voltage levels should be between the high (V_H) and low level (V_L) needed for the measuring circuit.

It is importnt to note that during the signal conditioning process is necessary to fit the pulse widths in such a way that the time of each pulse width is the same in both signals S_x and S_0.

After the signal conditioning process is complete the sensor's

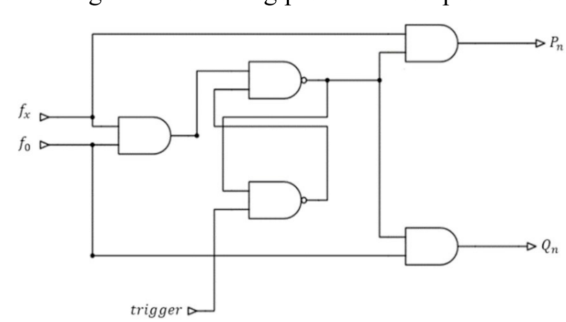

Fig. 4. Coincidence detector circuit.