Chinese Chemical Letters 26 (2015) 1022–1025

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Original article

Monitoring iodine adsorption onto zeolitic-imidazolate framework-8 film using a separated-electrode piezoelectric sensor

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A R T I C L E I N F O

Article history:
Received 5 January 2015
Received in revised form 19 March 2015
Accepted 3 April 2015
Available online 29 April 2015

Keywords:
Separated-electrode
Piezoelectric sensor
Iodine adsorption
Zeolitic-imidazolate framework

A B S T R A C T

In this work, a separated-electrode piezoelectric sensor (SEPS), constructed by a naked quartz crystal mounted between two electrodes, is reported for applications in a corrosive gaseous phase. The response of SEPS was measured by an impedance analysis method. It was shown that SEPS has an excellent frequency stability because its quality factor is in the order of 10^5. The SEPS can be operated even with the electrode gap in air larger than 1 cm. Compared with a conventional quartz crystal microbalance, the resonant frequency of the SEPS is independent of the mass change in the electrode. The SEPS was applied to monitor the adsorption of iodine on quartz surface and zeolitic-imidazolate framework-8 (ZIF-8) film as well as in the transfer of iodine between two ZIF-8 films. The SEPS offers the advantages of easy preparation, corrosion-resistant and convenience in combination with mass and optical measurements.

1. Introduction

Quartz crystal microbalance (QCM) is a useful tool for detection the mass change at the electrode surface in real time [1–3]. Usually, a QCM sensor is constructed with an AT-cut piezoelectric quartz crystal (PQC) disk sandwiched between two metal film electrodes, which induce the PQC resonator to oscillate at a frequency in the MHz. When an ultrathin, homogeneous and rigid mass loading is deposited on the electrode surface, a relationship between the frequency shift (ΔF) and mass change (Δm) is expressed by the Sauerbrey equation [4].

$$\Delta F = -2.26 \times 10^{-6} f_0^2 \frac{\Delta m}{A} \quad (1)$$

where f_0 and A are the fundamental frequency and electrode area of the QCM, respectively.

Metal-organic frameworks (MOFs), a particular class of ordered porous solids, hold promise to solve many key challenging societal needs (*e.g.*, hydrogen storage, carbon dioxide capture, renewable catalysts, controlled drug delivery) [5–11]. Recently, QCM is applied to characterize the adsorption of MOFs films [12–16]. In this work, a modified QCM sensor, separated-electrode piezoelectric sensor (SEPS), was used to monitor the adsorption process of iodine vapor on zeolitic-imidazolate framework-8 (ZIF-8) film. The motive of design SEPS is to eliminate the influence of the electrode corrosion by I_2 on the measurement of the resonant frequency. In the configuration of an SEPS (Fig. 1A), a naked PQC disk is mounted between two electrodes with a total air gap of several millimeters. The high-frequency excitation field is applied to the PQC resonator by the conductance of the air layer. The mass change on the separated-electrodes does not change the resonant frequency of the PQC resonator anymore. The influence of the electrode gap on the response of the SEPS was investigated by an impedance analysis method. The transfer of iodine between two ZIF-8 films was monitored by a series combination of two SEPS sensors.

2. Experimental

A schematic representation of the experimental setup is illustrated in Fig. 1. AT-cut 6.03 MHz quartz crystal discs with diameter of 14 mm were purchased from Beijing Chenjing Electronics Co., Ltd. (China). Two copper discs (with a diameter of 8 mm) were used as the excitation electrodes. A PQC disk was held by the bottom electrode with the help of a glass plate. The distance between the upper electrode and PQC was measure by a magnifier with scale. The electrodes were connected to a precision impedance analyzer (4294A, Agilent) by coaxial-cables. The resonant frequency and the intensity of the resonant peak were measured. In the experiment of iodine adsorption, ZIF-8 film was

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http://dx.doi.org/10.1016/j.cclet.2015.04.029

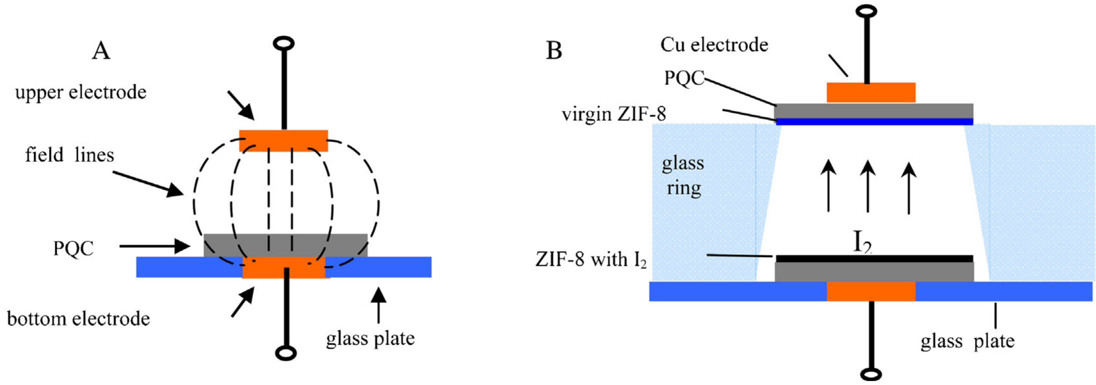

Fig. 1. Schematic drawing of the configuration of the SEPS (A) and experimental setup for the measurement of iodine transfer (B) (not to scale) for ZIF-8.

grown on one of the PQC surface by contact with the mixture of 25 mmol/L zinc nitrate and 50 mmol/L 2-methylimidazole in methanol. Then the SEPS with upwards ZIF-8 film was mounted in a sealed glass box. The electrode gap was *ca.* 2 mm. With the frequency of the blank quartz resonator as the reference, the frequency decrease of SEPS with ZIF-8 film was measured to estimate the mass of film grown. The thickness of the film was calculated from the mass per area by using the density of 0.95 g/cm^3 [17].

The adsorption was started by adding 20 mg I_2 (in 1 g NaCl powder) in the box. In the experiment for iodine transfer, a series combination of two SEPS sensors was employed (Fig. 1B) and their resonant frequencies were measured in two independent scans. Prior to I_2 transfer, a PQC with ZIF-8 film was exposed to saturated I_2 vapor for 3 h and then mounted on the bottom of the cell. Immediately, the glass ring (with a thickness of 2 mm) coved by another PQC with a virgin ZIF-8 film were added. The amounts of I_2 adsorbed or desorbed were calculated from the frequency shifts of the SEPS sensors.

3. Results and discussion

3.1. Influence of the electrode gap on the response of SEPS

As shown in Fig. 2A, a symmetrical resonant peak occurs in the conductance-frequency curve of the SEPS. The frequency at maximum conductance (G_{max}) is corresponded to the resonant frequency of the SEPS (f_{max}). Because of the high impedance of the air layer, the value of G_{max} in the SEPS is much less than that in a conventional QCM in air (30–200 mS). But the width of the resonant peak at half of the peak height, $f_2 - f_1$, is only 28 Hz. Accordingly, the quality factor of the SEPS, calculated by $Q = f_{max}/(f_2 - f_1)$, is as high as 2.2×10^5, which is close to that of a conventional QCM with the same dimensions. With increasing electrode gap, the value of G_{max} in SEPS is decreased remarkably (Fig. 2B). However, that the quality factor of SEPS is reduced slightly (data were not shown). For example, $Q = 7.9 \times 10^4$ was measured in the case with an electrode gap of 12 mm. The high quality factor in SEPS is reasonable because the air layer can be equivalent to a capacitor with little energy loss in conducting excitation field. On the other hand, the resonant frequency of the SEPS is independent of the mass change in the electrode. Because the resonant frequency of the SEPS increases with increasing electrode gap, it is essential to maintain a constant electrode gap in its applications. The SEPS with a shorter electrode gap is favorable to improve the signal-to-noise ratio in the measurement of resonant frequency. In fact, a conventional QCM may be considered as a special SEPS with zero electrode gap. By used an extrapolation, f_{max} = 6.046052 MHz and G_{max} = 87.2 mS were obtained at zero gap size. With the constant dimension and position of the electrodes used, the Sauerbrey equation in Eq. (1) is also valid

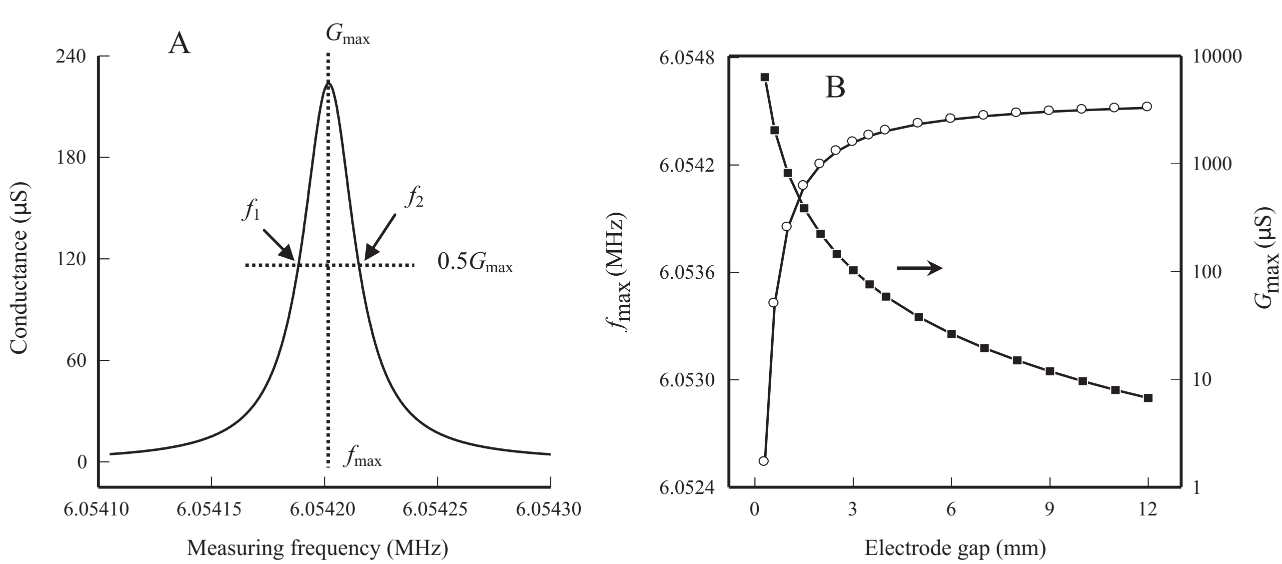

Fig. 2. Conductance-frequency curve of SEPS with electrode gap of 2 mm (A) and dependence of the resonant frequency and intensity of the resonant peak of SEPS on the electrode gap (B).