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Ionic liquid thin layer EQCM explosives sensor

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ABSTRACT

An integrated sensor that combines electrochemical and piezoelectric transduction mechanisms into a single miniaturized platform was developed and validated for the detection of nitro aromatic compounds such as ethyl nitrobenzene (ENB) and dinitrotoluene that are analogues of redox active explosives. An ionic liquid (IL) $BMIBF_4$ was used as both the electrolyte and the sorption solvent for the two-dimensional electrochemical and piezoelectric gas sensors.

The electrochemical behaviors of these nitro compounds in $BMIBF_4$ were studied by cyclic voltammetry, differential pulse voltammetry and square wave voltammetry, in parallel. The electrochemical properties of these compounds resembled the electrochemical reduction processes in their aprotic solutions, showing first a reversible reduction process and then subsequently an irreversible reduction processes. The redox properties of these compounds also depend on the number of nitro groups and the position of the nitro groups on the benzene ring. Square wave voltammetry was used to quantitatively analyze the ENB in $BMIBF_4$. Reduction peaks in the square wave voltammetric curves could be obtained when the concentrations were at ppm level. A small amount of moisture in the IL electrolyte did not significantly affect the redox behaviors. Piezoelectric quartz crystal microbalance (QCM) electrodes and the electrodes for amperometry were fabricated on a single piece of quartz plate. Detection of the volatile ENB vapor with this integrated EQCM chip was tested with both QCM and amperometric methods. The sensor's signal was related quantitatively to the ENB vapors adsorbed in $BMIBF_4$ from air. Combining amperometric and QCM detection simultaneously can cross-validate the detection technology, reduce false positives and false negatives and increase the accuracy of the detection.

1. Introduction

Gas sensors are of increasing interest due to their potential applications in ambient air monitoring, occupational health and safety, biomedical diagnostics, industrial process control, and security. Electrochemical (EC) sensors have historically proven to be very effective for measurement of airborne trace compounds. However, they are also known to suffer from interference and limited specificity. Similarly, piezoelectric gas sensors are very sensitive but are typically not very selective. To overcome these critical limitations of existing technology, in this report, we have developed an integrated sensor that combines electrochemical and piezoelectric transduction mechanisms into a single miniaturized platform. The piezoelectric electrodes for mass sensing and the electrochemical electrodes for amperometric detection were fabricated on a single quartz plate, allowing two-dimensional sensing *via* two orthogonal detection methods: quartz crystal microbalance (QCM) sorption and amperometric electrochemical reactivity. Simultaneous sensing with these two orthogonal methods provides additional selectivity to the sensor and significantly increases the accuracy of the detection at little or no power cost. This multidimensional sensing takes advantage of the unique properties of ionic liquids to realize both the electrolyte for amperometric detection and the sorption material for piezoelectric QCM detection, enabling a single gas sensor with enhanced sensitivity, specificity, and stability.

Amperometric sensors require the use of an electrolyte, an ionically conducting medium, to transport charge within the electrochemical cells, contact all electrodes effectively, and solubilize the reactants and products for efficient mass transport. Similarly QCM mass sensors require the use of a selective coating or film over the electrodes to absorbed gas into the film and generate a mass change. Ionic liquids (ILs) satisfy the requirements for both the electrolytes and the selective sorption coatings, permitting two-dimensional electrochemical and piezoelectric gases sensing from a single device. ILs have high ion conductivity, wide potential window (up to 5.5 V), high heat capacity and good chemical and electrochemical stability. They have been explored as media in electrochemical devices including super capacitors, fuel cells,

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lithium batteries, photovoltaic cells, electrochemical mechanical actuators and electroplating [1–4]. A small amount of water moisture absorbed in ionic liquids has been shown to have little effect on the electrochemical behavior of ionic liquid electrolytes [2]. ILs have negligible vapor pressure and thus low risk of drying out of the electrolytes. ILs are stable at relative high temperature (up to 350 °C), so most volatile organic contaminates could be removed by increasing the temperature of the system. Moreover, due to the excellent thermal stability of ILs, the problem of fouling by organic compounds and water moisture could be easily minimized or eliminated by heating to regenerate the ionic liquid-based sensors.

To validate the two-dimensional sensing approach, explosives with nitro (–NO_2) groups such as TNT were selected as target analytes because they have been used extensively to make homemade bombs. The increasing incidents and threats of terrorist attacks by improvised explosive devices have been the driving force to develop highly sensitive, specific and fast detection explosives sensor devices and systems. Many chemical sensing materials and detection devices for explosives detection have been developed [5–8]. The nitro (–NO_2) groups in most explosive compounds can be reduced electrochemically at a negative potential where most of aqueous electrolyte solutions are not stable [9–11]. However, when ionic liquids are used, the reductions of nitro compounds can be clearly observed and investigated without any decomposition of the ionic liquid electrolytes. A series of reports on amperometric detection of explosive materials has been published [12–26]. Direct sampling of explosives is very difficult because explosives are often being concealed. Most of the current techniques for explosive detection are based on the detection of explosive vapors because most organic nitro compounds, solid or liquid, have a measurable vapor pressure at room temperature. However, some explosive materials, such as 2,4,6-trinitrotoluene (TNT), have very low vapor pressure at room temperature. Mass produced TNT always has mono- or bi-substituted toluenes as impurities that are quite volatile at room temperature [27]. Therefore, detection of ethyl nitrobenzene (ENB) and dinitrotoluene (DNT) vapors as analogues of TNT and other explosives could be an effective alternative. We have developed ionic liquid-based QCM sensors for detection of volatile organic compounds [28,29] including ENB and DNT. QCM/IL sensors have shown sensitivities as low as 115 ppm for methane at room temperature [28]. However, a QCM/IL sensor alone often cannot provide the selectivity needed for identification of any specific vapor analyte. Previously, QCM/IL sensor arrays were used for classification (identification) of volatile organic compound vapors, such as ethanol, benzene, or dichloromethane [28–30]. In this paper, the electrochemical behavior of ENB and DNT was first investigated in bulk ionic liquid solutions. Then, QCM and electrochemical sensing methods were tested separately on a standard QCM device and a thin-layer electrochemical setup on glass slide. Finally, QCM electrodes and the electrodes for amperometry were fabricated together on a single piece of quartz to produce an integrated electrochemical quartz crystal microbalance (EQCM) chip. Detection of volatile ENB vapor was tested using both QCM and amperometric methods with this new integrated chip. The results demonstrate that the EQCM sensor chip performed excellently both as a QCM sensor and as an amperometric sensor. This integrated, two-dimensional sensing technology permits reduction or elimination of false positive or false negative results and significantly increases the accuracy of the detection. The integrated device permits miniaturization, effectively reducing the size and number of the parts required for electrochemical and QCM detection, and supports lab-on-chip analytical chemistry. Furthermore, ionic liquids are proven to be a unique material that satisfies the requirements of both detection methods, being a gas absorption material for QCM and a molten electrolyte for amperometry.

2. Chemicals and methods

2.1. Chemicals

Ionic liquid butylmethylimidazolium tetraflouroborate ($BMIBF_4$) was purchased from Acros Inc. with over 98% purity and used as received. Ethylnitrobenzene (ENB), 2,4-dinitrotoluene (2,4-DNT), 3,4-dinitrotoluene (3,4-DNT), and 2,6-dinitrotoluene (2,6-DNT) were purchased from Aldrich Inc. and also used as received without any further purification.

2.2. Electrodes

Concentric rings-disk electrode (RsDE) devices were prepared by vapor deposition of 5-nm of Ti followed by 100-nm of Au on glass slides. Then photolithography and wet etching were applied to pattern of the electrodes as shown in Fig. 1A. The disk electrode in the center has a diameter of 2.54 mm. The disk electrode is surrounded by three concentric ring electrodes, each with an opening on the same side for wiring. The first, second, and third rings are 0.7 mm, 0.5 mm, and 0.75 mm wide, respectively. The gap between the first and the second ring electrodes and the second and the third electrodes are 50 μm and 250 μm, respectively. The disc electrode was used as quasi reference electrode. The first and the second rings were used as working and counter electrodes, respectively. This choice of electrode allows the working electrode and counter electrode to be close together so that the IR drop can be reduced. Additionally, the quasi-reference electrode and the counter electrode are placed far apart to prevent the product at the counter electrode to diffuse to the reference electrode and affect reference electrode stability.

The EQCM device shown in Fig. 1B was prepared using the same methods as the RsDE device, with the RsDE pattern on one side of a quartz plate. The other side of the quartz plate was coated with a gold disk electrode. The two disk electrodes overlapped concentrically. Our experience shows that the gold and non-polished quartz plate substrates are very wettable by ionic liquid $BMIBF_4$. When the RsDE was used, 4 μL of $BMIBF_4$ or its solutions were pipet-

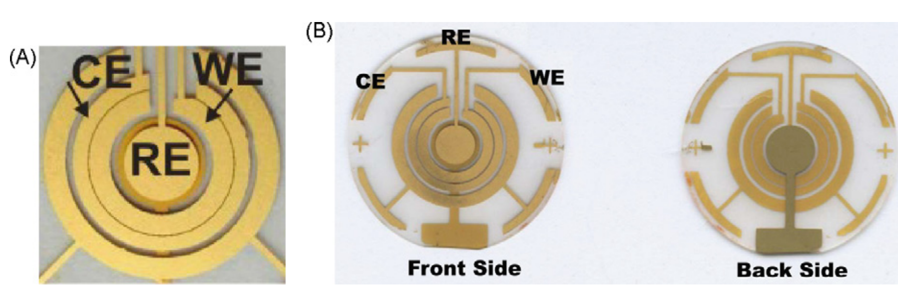

Fig. 1. (A) Pattern of electrodes on an RsDE and (B) on front and back sides of an EQCM electrode.