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Nafion-Indium Tin Oxide composite Quartz Crystal Microbalance Sensor for Polar and Non-Polar Vapors

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Abstract: The development of electronic noses has been an active area of research in recent years. Human sense of smell is subjective, has poor reproducibility due to such factors as fatigue and prior odors analyzed, and should not be used to detect potentially toxic chemicals. Electronic noses do not have these restrictions and offer the potential to produce reliable measurements. Electronic noses have numerous applications such as identifying toxic vapors or explosive chemicals in a warfare or factory environment, sniffing for illicit drugs, and determining food quality control and spoilage. One such electronic nose is a quartz crystal microbalance, in which a coating on a quartz crystal surface selectively interacts with vapors of interest, resulting in a change in oscillation frequency of the quartz crystal. One major category of chemical compound vapors is that they can be either polar or non-polar. In this study, we construct a quartz crystal with a nanocomposite coating that aids in determining if a vapor source is from a polar or non-polar chemical source.

Keywords: Quartz crystal microbalance, Indium tin oxide, Nafion, Nanocomposites, Electronic nose.

1. Introduction

Nafion®, as shown in Fig. 1 [1] was developed at DuPont Inc. during the 1960's by modifying Teflon®.

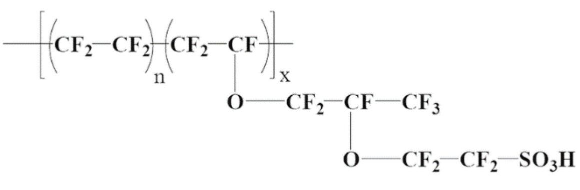

Fig. 1. Chemical structure of Nafion $(C_7HF_{13}O_5S \cdot C_2F_4)_x$

It is a sulfonated tetrafluoroethylene-based fluoropolymer-copolymer [2]. Nafion was the first synthetic polymer ever developed with ionic properties and started an entirely new class of polymers called ionomers [3]. Organic-inorganic nanocomposites have been regarded as a new class of materials with many novel electronic, optic, and magnetic applications [4]. Composites can be made by several methods such as mixing metal oxides with polymers. In this study, the properties of the organic polymer Nafion are combined with the properties of the metal oxide Indium-Tin Oxide (ITO) on the surface of a quartz crystal to study mainly organic vapors. Nafion absorbs organic vapors very easily. It has been demonstrated that a Nafion-coated Quartz Crystal Microbalance (QCM) can be used as an extremely sensitive method for the study of organic vapors [5].

In chemistry, polarity refers to the distribution of electric charge across a molecule. Polar molecules have an asymmetrical charge distribution. Non-polar molecules have a more symmetrical charge distribution. Polarity underlies several physical properties of a chemical, including surface tension, solubility, and melting and boiling points. Solvents can be broadly classified as being polar or non-polar. Generally, the dielectric constant of the solvent provides a rough measure of a solvent's polarity. Solvents with a dielectric constant of less than 15 are generally considered non-polar [6].

Fig. 2 shows the chemical structure of the vapor samples used in this study with the Nafion-ITO nanocomposite QCM sensor. Note that the polar samples have an asymmetrical chemical structure, while the non-polar samples, except for toluene have a symmetrical chemical structure.

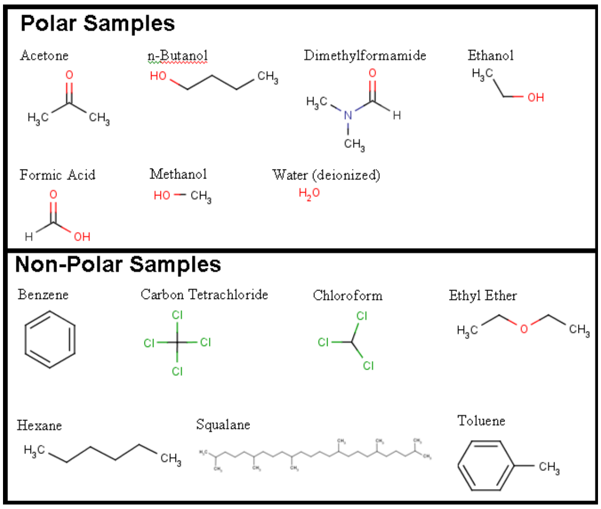

Fig. 2. Chemical structure illustrations of samples used in this study.

Table 1 shows a list of the samples measured in this study, along with molecular weight, vapor pressure, and dielectric constant data for each [7].

Table 1. Molecular weight, vapor pressure, and dielectric constant(κ) data of samples used in this study.

	Molecular Weight (g/mol)	**Vapor Pressure (mm Hg, 25°C)**	**κ**
Polar Samples			
Acetone	58.08	232	21
n-Butanol	74.12	6.7	18
Dimethylformamide	73.09	3.87	38
Ethanol	46.07	59.3	30
Formic Acid	46.02	42.6	58
Methanol	32.04	127	33
Water (deionized)	18.01	23.8	80
Non-Polar Samples			
Benzene	78.11	94.8	2.3
Carbon Tetrachloride	153.82	115	2.2
Chloroform	119.38	197	4.8
Ethyl Ether	74.12	583	4.3
Hexane	86.18	151	2
Squalane	422.82	0.000275	NA
Toluene	92.14	28.4	2.4

2. Experimental

Experimental details about the deposition of ITO on the quartz crystal, and structural studies of ITO films using the scanning electron microscope were reported earlier [8]. The quartz crystal microbalance (QCM) sensor in this study comprises a quartz crystal coated with a chemically sensitive Nafion-ITO nanocomposite thin film. The crystal has a fundamental frequency of 5 MHz. When vapors from the sample interact with the Nafion-ITO nanocomposite thin film, a change in resonance frequency is observed. The Nafion-ITO nanocomposite quartz crystal was prepared by pipetting 5μL of a 5% Nafion by weight solution in lower aliphatic alcohols and water on to the AT-cut gold quartz crystal, spreading it evenly, and allowing it to evaporate very slowly for 12 hours. The Nafion-ITO nanocomposite layer has an area of 1.766 cm^2 on the quartz crystal and has a colorful surface, as shown in Fig. 3.

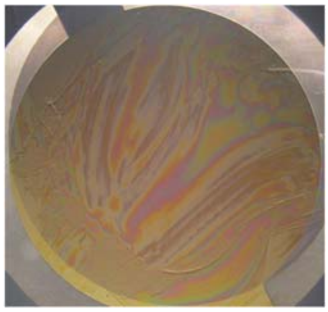

Fig. 3. Optical microscope picture Nafion + ITO nanocomposite on surface of gold quartz crystal.

The quartz crystal microbalance (Stanford Research Systems, Model: QCM200) was used to simultaneous measure the change in the frequency as well as the change in the surface resistance of a sensitive layer of Nafion-ITO nanocomposite thin films deposited on the quartz crystal of the QCM in the presence of the sample vapor. 15 μL of either a polar or non-polar solvent was applied over one end of a 20 cm length, 2 cm width and 0.3 mm thick paper strip. The paper strip with the absorbed liquid sample was inserted immediately in the open glass jar and kept 1cm above the surface of the Nafion-ITO nanocomposite film for 20 seconds, and then removed from the jar. A digital timer was used to measure the 20 second period. A new paper strip was used for each run of each test sample. All measurements were performed in the laboratory at a temperature of approximately 21 °C and at approximately 50 % relative humidity.

3. Results and Discussion

Fig. 4 shows the average of five 20 second sample exposure, Nafion-ITO nanocomposite QCM sensor change in frequency measurements for all tested samples.

All the non-polar vapor samples show an overall QCM sensor increase in frequency with the Nafion-ITO nanocomposite crystal, except for the squalane sample, which shows a slight decrease. All the polar vapor samples show an overall QCM sensor decrease in frequency with the Nafion-ITO nanocomposite crystal. Also, all the non-polar vapor samples show a much faster QCM sensor return to frequency baseline time than the polar vapor samples. The QCM sensor change in frequency responses to the non-polar and polar vapor samples are shown separately in Figs. 5 and 6 respectively.

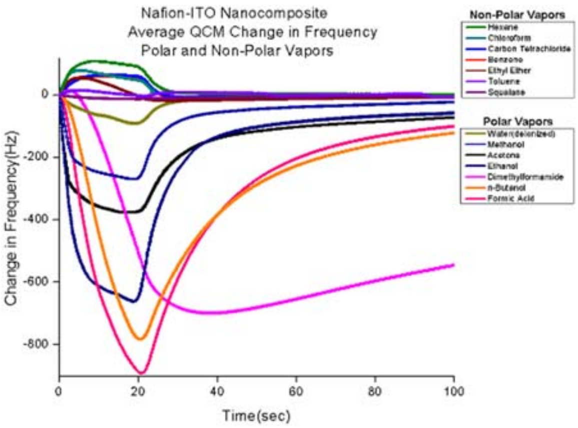

Fig. 4. Average Nafion-ITO nanocomposite QCM sensor change in frequency responses to polar and non-polar vapor samples.

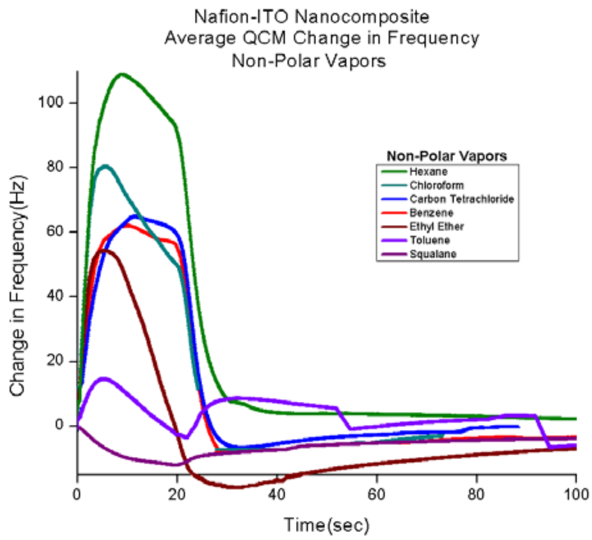

Fig. 5. Average Nafion-ITO nanocomposite QCM sensor change in frequency responses to non-polar vapor samples.

Among the non-polar vapor samples, hexane showed the greatest Nafion-ITO nanocomposite QCM sensor average increase in frequency response in Fig. 5.

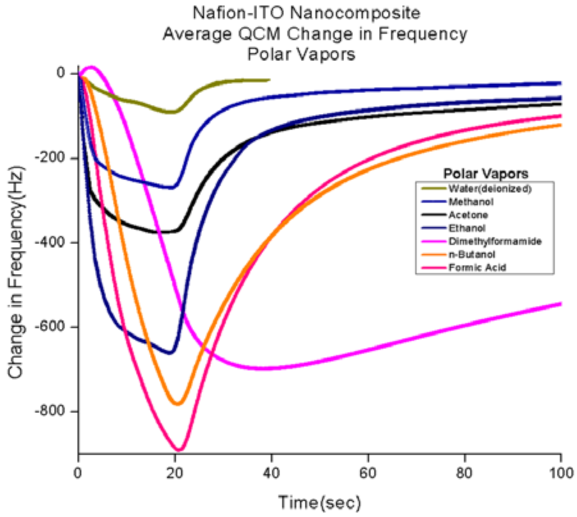

Fig. 6. Average Nafion-ITO nanocomposite QCM sensor change in frequency responses to polar vapor samples.

Among the polar vapor samples, deionized water showed the lowest Nafion-ITO nanocomposite QCM sensor average decrease in frequency response, while formic acid showed the highest Nafion-ITO nanocomposite QCM sensor average decrease in frequency response in Fig. 6.

Fig. 7 shows the average of five 20 second sample exposure, Nafion-ITO nanocomposite QCM sensor change in surface resistance measurements for all samples.

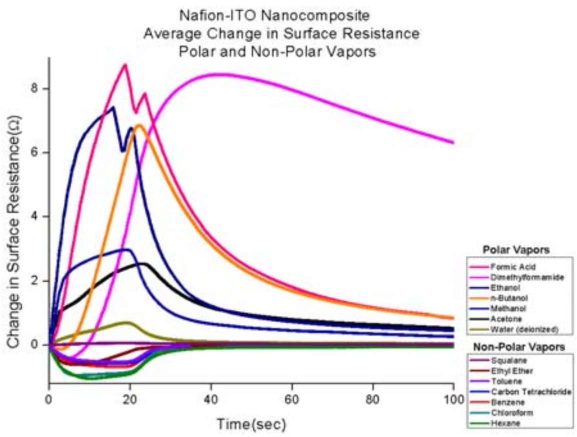

Fig. 7. Average Nafion-ITO nanocomposite QCM sensor change in surface resistance responses to polar and non-polar vapor samples.

All the non-polar vapor samples show an overall QCM sensor decrease in surface resistance with the Nafion-ITO nanocomposite crystal, except for the squalane sample, which shows a slight increase. All the polar vapor samples show an overall QCM sensor increase in surface resistance with the Nafion-ITO nanocomposite crystal. Also, all the non-polar vapor samples show a much faster QCM sensor return to surface resistance baseline time than the polar vapor samples. The QCM sensor change in surface resistance responses to the polar and non-polar vapor samples are shown separately in Figs. 8 and 9 respectively.

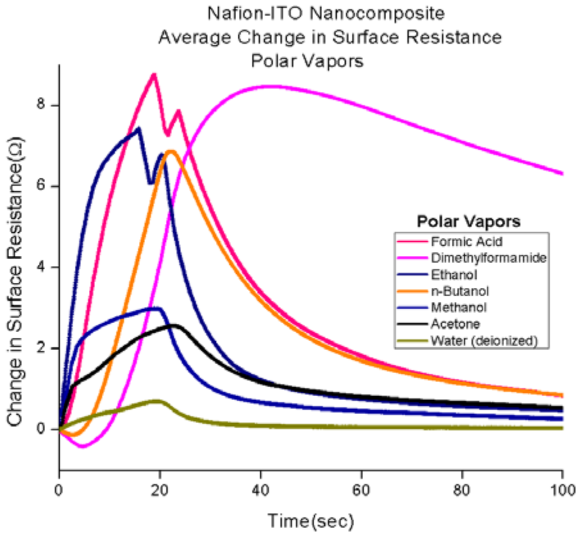

Fig. 8. Average Nafion-ITO nanocomposite QCM sensor change in surface resistance responses to polar vapor samples.

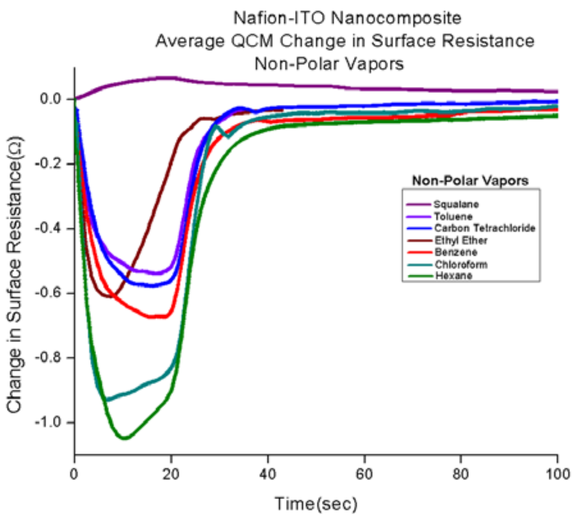

Fig. 9. Average Nafion-ITO nanocomposite QCM sensor change in surface resistance responses to non-polar vapor samples.

Among the polar vapor samples, deionized water showed the lowest Nafion-ITO nanocomposite QCM sensor average increase in surface resistance response, while formic acid and dimethylformamide showed the highest Nafion-ITO nanocomposite QCM sensor average increase in surface resistance response in Fig. 8.

Among the non-polar vapor samples, hexane showed the largest Nafion-ITO nanocomposite QCM sensor average decrease in surface resistance response in Fig. 9.

Theoretical explanations for the observed Nafion-ITO nanocomposite QCM sensor decrease in frequency with polar sample vapors and increase in frequency with non-polar sample vapors are still being investigated. The Nafion-ITO nanocomposite QCM sensor decrease in frequency observed with the polar sample vapors indicates an increase in mass on the sensing surface of quartz crystal microbalance. The Nafion-ITO nanocomposite QCM sensor increase in frequency observed with the non-polar sample vapors indicates a decrease in mass on the sensing surface of on the quartz crystal microbalance. Randová et. al. [9] reported that Nafion preferentially absorbs polar over non-polar vapors, which is consistent with our results.

Also, theoretical explanations for the observed Nafion-ITO nanocomposite QCM sensor increase in surface resistance with polar sample vapors and decrease in surface resistance with non-polar sample vapors are also still being investigated. The Nafion-ITO nanocomposite QCM sensor increase in surface resistance observed with the polar sample vapors indicates an increase in viscoelasticity on the sensing surface of on the quartz crystal microbalance. The Nafion-ITO nanocomposite QCM sensor decrease in surface resistance observed with the non-polar sample vapors indicates an increase in rigidity, or a decrease in viscoelasticity on the sensing surface of on the quartz crystal microbalance [10].

4. Conclusions

The Nafion-ITO nanocomposite QCM sensor was sensitive to polar and non-polar vapors in this study. The Nafion-ITO nanocomposite QCM sensor showed a predominate increase in frequency with non-polar vapors, and a predominate decrease in frequency with polar vapors. The Nafion-ITO nanocomposite QCM sensor showed a predominate increase in surface resistance with polar vapors, and a predominate decrease in surface resistance with non-polar vapors. The Nafion-ITO nanocomposite QCM sensor displayed an impressive ability to distinguish between polar and non-polar sample vapors, which could be utilized as part of an electronic nose sensor array. The Nafion-ITO nanocomposite QCM sensor's ability to distinguish between polar and non-polar organic sample vapors suggests that other sample vapor chemical properties such as being protic or aprotic, hydrophobic or hydrophilic, or aliphatic or aromatic could also possibly be distinguished based on the observed QCM sensor changes in frequency and/or changes in surface resistance with other quartz crystal coatings or composites.

Acknowledgements

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