Measurement of Methanol Solutions Using Love Mode Liquid Sensor

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Abstract—Controlling the methanol concentration is a key factor in improving the efficiency of the direct methanol fuel cell. In this study, the immersed-type Love mode sensor based on SiO$_2$/ST-cut Y-propagation quartz was fabricated for monitoring the methanol concentration. A temperature controlled measurement system consisting of a spectrum analyzer and an oscillator circuit was employed to characterize the methanol solutions with different weight concentrations at different temperatures. A theoretical prediction of the phase velocity shift for the methanol solutions with different weight concentrations was also performed for comparison. The results of methanol solutions with different weight concentrations at different temperatures show that the amount of the frequency shift is approximately linearly proportional to the weight concentration, and the proportional rate increases as the temperature increases. The concentration resolutions were 1.1876 and 0.2484 %/kHz by weight at 25°C and 70°C.

Keywords—love wave; sensor; methanol concentration; DMFC

I. INTRODUCTION

Surface acoustic wave (SAW) devices have been widely used in a variety of sensors because SAW devices possess many advantages, such as compact size, high integration, rigid structure, good sensitivity toward surface perturbations, and ease of mass production. Several types of SAWs, such as shear horizontal SAW (SH-SAW) and Love wave, are not coupled elastically with liquids and therefore these types of SAWs are suitably applicable for liquid sensing [1–7]. Love wave can be generated in the layered structure comprising a piezoelectric substrate and an upper layer with low acoustic wave velocity. Then, the acoustic wave will be confined and travelling in the form of horizontal polarized shear wave in the upper layer, for this reason, the layer is so-called guiding layer. The guiding layer not only acts as a waveguide which is sensitive towards the surface perturbations but also protects the interdigital transducers (IDTs) from corruptions when operating in aqueous samples. Sensitivity of Love mode liquid sensors significantly depends on the operating frequency as well as properties of thickness and material of guiding layers [8].

Direct methanol fuel cell (DMFC) is a promisingly alternative energy owing to the merit of ease of refueling, harmless storage, and high power density [9-14]. Controlling the methanol concentration in the inlet of the fuel flow at anode side or in the mixing tank is very important to maintain the energy efficiency, durability, and performance of the fuel cell [6]. Operating in a low methanol concentration causes low energy efficiency and poor stability. High concentration of methanol is required to reduce the anode overpotentials, which are lowering the cell voltage [9, 14]. However, in this situation, the methanol crossover also occurs and induces a mixed potential in the cathode to worse the performance simultaneously. Thus, monitoring methanol concentration is a crucial factor to maintain high efficiency and good stability of DMFC. An adequate methanol concentration of 3% by weight (1 M) is widely used in DMFCs [12]. To monitor the methanol concentration, some principles based on electrochemical properties and physical properties had been discussed [11]. The physical methanol concentration sensor is reliable, robust, and wide measurement range. In such physical approaches, the SAW sensors without coating reactive films may be a promising candidate. By utilizing the MicroElectroMechanical Systems (MEMS) with the high-resolution photolithography or employing the high speed layered structure, the miniaturized SAW sensors are suitable for embedding in fuel cell for instantaneous detection.

In this study, the immersed-type Love mode liquid sensor based on SiO$_2$/ST-cut Y-propagation quartz for determining the methanol concentration were investigated, theoretically and experimentally. In numerical simulations, the change of the phase velocity of Love mode sensors with different methanol
concentration was evaluated. In experiments, the immersing measurement was adopted for three advantages as follows. First, the sensor can be integrated with fluid channel easily and, hence, the change of concentration can be monitored instantaneously. Second, the temperatures of sensor and fluid sample are the same and therefore the inaccuracy caused by temperature effects can be avoided. Moreover, the influences of the environment of common laboratory on sensors can be vanished. Measurement on various weight concentrations of methanol solutions at different temperatures was performed. The concentration resolutions for different temperatures were presented. The results show that the concentration resolutions are proportional to the temperature. A SH-SAW sensor also fabricated on the ST-cut Y-propagation quartz and measured for comparison. Results indicated that the fabricated Love mode sensor exhibits the higher sensitivity than the fabricated SH-SAW sensor.

II. NUMERICAL SIMULATION

The Love mode liquid sensor considered in this study consists of ST-cut Y-propagation quartz (z < 0), fused silica (SiO$_2$) (0 < z < h), and methanol solution (z > h). The acoustic and electric fields in quartz and SiO$_2$ can be expressed as [15-17]

\[ u_j^{(1)} = \sum_{m=1}^{2} C_m a_j^{(m)} \exp(ikb^{(m)}z) \exp[i(kPX-vt)], \quad j = 2, \]

\[ \phi_j^{(1)} = \sum_{m=1}^{2} C_m a_j^{(m)} \exp(ikb^{(m)}z) \exp[i(kPX-vt)], \]

\[ u_j^{(2)} = \sum_{m=1}^{4} X_m a_j^{(m)} \exp(ik\beta^{(m)}z) \exp[i(kPX-vt)], \]

\[ \phi_j^{(2)} = \sum_{m=1}^{4} X_m a_j^{(m)} \exp(ik\beta^{(m)}z) \exp[i(kPX-vt)], \]

where \( u \) is the acoustic displacement, \( \phi \) the electric potential, \( v \) the phase velocity, \( k \) the wave number in the y-direction, \( P = 1 + jy \), \( \gamma \) the attenuation coefficient, \( b \) and \( \beta \) the wave number ratios, \( a \) and \( \alpha \) the corresponding eigenvectors, and \( C \) and \( X \) the associated partial field amplitudes. Substituting (1) and (2) into stiffened Christoffel equations, which describe the acoustic and electric field behavior in a piezoelectric substrate, yields a fourth-degree algebraic equation in the wave number ratio \( b \). There are four real or complex values of \( b \) can be derived from each pair of values of \( (v, \gamma) \). For a semi-infinite piezoelectric substrate, ST-cut Y-propagation quartz in this case, two complex roots with a negative imaginary part is selected. All four roots of \( \beta \) are selected for SiO$_2$.

The boundary conditions require that the acoustic displacements and stresses be continuous at \( z = 0 \), and a stress-free surface is assumed at \( z = h \). In addition, the electric potential and the normal component of electric displacement must be continuous at the interface for an electrically free surface. For a metalized (thin metal film) surface, the electric potential disappears. Substituting (1) – (4) into the boundary conditions, the phase velocity \( v \) and the attenuation coefficient \( \gamma \) can be obtained numerically. The coupling coefficient \( K^2 \) can then be calculated from

\[ K^2 = \frac{(v_f - v_m)}{v_f}, \]

where \( v_f \) and \( v_m \) are phase velocities obtained when the electrical boundary conditions at the interface at which the IDT is placed are assumed to be electrically free and shorted, respectively. In this study, the effects of the electric properties of methanol solutions such as dielectric constant on the phase velocity of Love wave are considered, and the effects of viscosity ignored. The material constants used in this study are obtained from Albright et al. [18, 19].

It is known that the oscillation frequency shift of sensors induced by the change of the methanol concentration is proportional to the velocity shift of SAWs, thus, the velocity shift of Love wave is calculated here to investigate the feasibility of Love mode sensors for methanol concentration monitoring. In addition, the effects of thickness of SiO$_2$ on phase velocity and coupling coefficient are also investigated. By employing the above-mentioned theoretical method, the maximum \( K^2 \) of 0.222% occurs at the SiO$_2$ thickness-to-wavelength ratio of 0.07, with a phase velocity of 4942.68 m/s. The SiO$_2$ thickness-to-wavelength ratio of 0.0416 adopted in the following experiment are also estimated, the associated \( K^2 \) and phase velocity are 0.199% and 4942 m/s, respectively. Figure 1 shows the calculated velocity shift with these two SiO$_2$ thickness-to-wavelength ratios, 0.0416 and 0.07, for different methanol concentrations. In Fig. 1, the dielectric constants of the methanol solutions with different methanol concentrations are taken into account [19]. The amount of velocity shift is proportional to coupling coefficient of the Love mode sensor. Moreover, the amount of velocity shift increases as the methanol concentration increases, the relationship becomes approximately linear for the methanol concentration less than 10% by weight. These results imply that Love wave sensor is applicable for the measurement of methanol concentration.

![Figure 1. The calculated velocity shift of the Love mode sensor with two different SiO2 thickness-to-wavelength ratios, 0.0416 and 0.07.](image)

III. EXPERIMENT

Figure 2 shows the schematic illustration of the fabricated immersed-type Love mode liquid sensor which consists of the
The input and output IDTs both have 80 finger pairs with the x direction. Single-electrode aluminum IDTs are adopted. The input and output IDTs is 16.5 mm. SiO2 is adopted as the guiding layer due to its good elastic and thermal properties as well as excellent physical and chemical stabilities. Additionally, SiO2 exhibits lower acoustic loss than other most commonly used polymers, such as polymethyl methacrylate (PMMA). SiO2 with a thickness of 5 μm was deposited on ST-cut quartz substrate by plasma enhanced chemical vapor deposition (Oxford Plasmalab System 100).

The experimental configuration comprising an oscillator amplifier, a signal spectrum analyzer, a data processing PC, and a Love mode sensor immersed in a liquid sample, which is supported by a sealed beaker on a heater. The beaker is filled with samples and sealed to prevent the evaporation phenomenon that causes the undesirable inaccuracy of measurement, especially at high temperature. The oscillation spectrum of the fabricated Love mode liquid sensor is measured by a standard signal spectrum analyzer (Agilent E4403) with a power supply (EPE ep5000). As the measured result, the operating frequency and effective phase velocity of the fabricated sensor is 37.076 MHz and 4450 m/s, respectively, with an insertion loss of 15.96 dB. The measured effective phase velocity is lower than the value of theoretical prediction. It may be attributed to the inaccuracy of the thickness or material constant of SiO2, the mass effects of IDTs, or other effects of fabrications.

IV. RESULTS AND DISCUSSIONS

The properties of materials are varying with temperature and, hence, the oscillation frequency of the Love mode sensor will be changed as the temperature changes. In this study, the shift of oscillation frequency is adopted to determine the methanol concentration. Therefore, the oscillation frequency of distilled water at 25°C was used as the reference to eliminate the effect of temperature on oscillation frequency for the following measurement.

Figure 3 represents the oscillation spectrums with different methanol concentrations at 25°C. The frequency shift increases with the increasing methanol concentration. Figure 4 shows the measured shifts of oscillation frequencies with different methanol concentrations at various temperatures. As the results in Fig. 4, the linear relationship for each temperature can be obtained. The correlation coefficients at 25, 50, 60, and 70°C are 0.99, 0.98, 0.94, and 0.95, respectively. An increase in the slope of fitting curve is revealed as the temperature increases. This result implies that the sensitivity increases as temperature increases. In other words, at the constant concentration, the higher the temperature, the larger the frequency shifts. The result can be attributed to the viscosity and dielectric constant of the water and methanol decreases as the temperature increases resulting in an increase in acoustic velocity as well as in frequency shift [7]. Also, the particle displacement increases with decreasing viscosity and therefore increases the frequency shift [3]. The concentration resolution measured by the time stability is also estimated in this work. The concentration resolutions of the sensor are 1.1876 and 0.2484 %/kHz by weight at 25°C and 70°C, respectively. According to the result, high operating temperature will improve the concentration resolutions of Love mode sensors.

The immersed-type SH-SAW sensor with operating frequency of 63MHz was fabricated on the ST-cut Y-propagation quartz for sensing the methanol concentration as the comparison with the results of Love mode liquid sensors. The input and output IDTs of the SH-SAW sensor was protected by the epoxy for immersing measurement. Measured frequency shift of fabricated SH-SAW sensor and Love mode sensor at room temperature are shown in Fig. 5. The Love mode sensor exhibits the higher sensitivity than SH-SAW sensor. It can be attributed that the fabricated SH-SAW sensor has the smaller coupling coefficient (0.017%) than the fabricated Love mode sensor (0.199%).

V. CONCLUSIONS

In this study, the immersed-type Love mode liquid sensor based on SiO2/ST-cut Y-propagation quartz was developed for detecting methanol concentration. A theoretical simulation was performed to investigate the effects of the thickness of SiO2 on the phase velocity and coupling coefficient of the Love mode sensor. The results show that the amount of velocity shift is
proportional to coupling coefficient of the Love mode sensor. Moreover, the amount of shift increases as the methanol concentration increases, the relationship becomes approximately linear for the methanol concentration less than 10% by weight. These results imply that Love wave sensor is applicable for the measurement of methanol concentration. The immersing measurement was employed not only to prevent the influences from environments of common laboratory but provides good accuracy and instantaneous detection. The results of methanol solutions with different weight concentrations at various temperatures show that the amount of the frequency shift is approximately linearly proportional to the weight concentration, and the proportional rate increases as the temperature increases. The concentration resolutions were approximately linear for the methanol concentration less than 10% by weight. These results imply that Love wave sensor is applicable for practical methanol detection in the DMFC system.

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