Development of Shear Horizontal Surface Acoustic Wave Sensor for Detecting Methanol Concentrations in a Direct Methanol Fuel Cell

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***Abstract*— A liquid phase sensor is realized by using a shear horizontal surface acoustic wave (SH-SAW). The SH-SAW sensor can detect density and viscosity product, conductivity and relative permittivity of liquid. Sensor sensitivity depends on a piezoelectric substrate used. When a 36° rotated Y-cut, X propagating $LiTaO_3$ is used for the substrate, high sensitive detection of electrical properties is possible. In this paper, the SH-SAW sensor is applied to a methanol (MeOH) sensor. First, frequency dependences of the SH-SAW sensor are discussed. The results indicate that the responses of high frequency sensor agree with the perturbation theory. The application of the SH-SAW sensor is MeOH concentration detection in a direct methanol fuel cell (DMFC). As a formic acid is produced during electrode reactions in the DMFC, real fuel becomes binary-mixture solutions of MeOH and formic acid. In this paper, the solutions are also measured. It is found that influence of the formic acid can be neglected by using high frequency SH-SAW sensor. This means that the MeOH concentration is determined from phase shift.**

Keywords-component; SH-SAW sensor; direct methanol fuel cel;, methanol senso; influence of sensor frequency

I. INTRODUCTION

Surface acoustic wave (SAW) devices have a wide range of applications not only in filters, resonators, and oscillators [1], but also in sensors [2] and actuators [3]. Propagating characteristics of a SAW depends on an adjacent medium on a SAW propagating surface. The SAW is mechanically and electrically perturbed, when the adjacent medium physically and chemically changes. When a liquid is loaded on the SAW propagating surface, the SAW is influenced by liquid properties, such as density, viscosity, conductivity, and permittivity. However, to realize a liquid-phase SAW sensor, it is necessary to use a shear horizontal SAW (SH-SAW) to avoid a longitudinal wave radiation into a liquid [4].

A direct methanol fuel cell (DMFC) [5] is operated using a methanol (MeOH) solution. The reactions on the anode and cathode in the DMFC are as follows:

$$CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2 \text{ for the anode,}$$

$$\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \text{ for the cathode.}$$

As the generation efficiency of the DMFC depends on the concentration of MeOH, the concentration must be known. As the DMFC has an optimum concentration range, monitoring of the MeOH concentration is required. The MeOH concentration is a function of sound speed, viscosity, density, permittivity, and refractive index. The SH-SAW sensor can detect viscosity and density products, and permittivity. The SH-SAW sensor, which is fabricated on 36° rotated Y-cut, X-propagating $LiTaO_3$ (36YX-$LiTaO_3$) can detect the permittivity with high sensitivity [6]. In previous research [6-9], frequency of the SH-SAW sensor was fixed at 50 MHz. In this paper, the SH-SAW sensors with different frequencies are used. The MeOH solutions are measured by changing the temperature. The experimental results are compared with the perturbation theory. Also, influence of a formic acid is discussed.

II. THEORY

Detection mechanism of the MeOH concentration is based on the electrical perturbation [10, 11]. A reference liquid is assumed as nonelectrolyte and expressed as

$$\varepsilon_\ell = \varepsilon_r \varepsilon_0. \qquad (1)$$

Here, ε_ℓ, ε_r, and ε_0 are dielectric constant, relative permittivity of the reference liquid, and dielectric constant of free space, respectively. Electrical property of a sample solution is represented by a complex permittivity, ε_ℓ', as follows.

$$\varepsilon_\ell' = \varepsilon_r' \varepsilon_0 - j\frac{\sigma'}{\omega} \qquad (2)$$

Here, σ is conductivity of liquid, ω is an angular frequency of the SH-SAW sensor, and $j = \sqrt{-1}$. The prime (′) denotes parameter of the sample solution. The SH-SAW is electrically perturbed the change from (1) to (2). The velocity shift, $\Delta V/V$, and attenuation change which is normalized by wave number, $\Delta\alpha/k$, are expressed by the following equations.

$$\frac{\Delta V}{V} = -\frac{K_s^2}{2}\frac{(\sigma'/\omega)^2 + \varepsilon_0(\varepsilon_r' - \varepsilon_r)(\varepsilon_r'\varepsilon_0 + \varepsilon_P^T)}{(\sigma'/\omega)^2 + (\varepsilon_r'\varepsilon_0 + \varepsilon_P^T)^2} \qquad (3)$$

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$$\frac{\Delta\alpha}{k} = \frac{K_s^{\ 2}}{2} \frac{(\sigma'/\omega)\left(\varepsilon_r\varepsilon_0 + \varepsilon_P^T\right)}{(\sigma'/\omega)^2 + \left(\varepsilon_r'\varepsilon_0 + \varepsilon_P^T\right)^2} \qquad (4)$$

Here, $K_s^{\ 2}$ is an electromechanical coupling coefficient when the reference liquid is loaded on the SH-SAW surface, and ε_P^T is an effective permittivity of the substrate used.

As a MeOH solution is nonelectrolyte, the conductivity can be neglected. Then, (3) and (4) become to

$$\frac{\Delta V}{V} = -\frac{K_s^{\ 2}}{2} \frac{\varepsilon_0\left(\varepsilon_r' - \varepsilon_r\right)\left(\varepsilon_r'\varepsilon_0 + \varepsilon_P^T\right)}{\left(\varepsilon_r'\varepsilon_0 + \varepsilon_P^T\right)^2}, \qquad (5)$$

$$\frac{\Delta\alpha}{k} = 0. \qquad (6)$$

Equations (5) and (6) show that the velocity shift does not depend on the frequency and the normalized attenuation change does not changed.

In this paper, the temperature of the SH-SAW sensor was varied. The electromechanical coupling coefficient, effective permittivity, and electrical properties of liquid depend on the temperature. The coupling coefficient is calculated from the phase velocities on free and shorted surfaces. The phase velocity can be calculated by extended Campbell and Jones method for liquid/piezoelectric substrate structure [4, 12]. Kushibiki's material constants [13] and Smith's temperature coefficients [14] of $LiTaO_3$ were used for the numerical calculation. Material constants of MeOH solution were obtained from the chemical handbook [15].

III. EXPERIMENTAL PROCEDURE

A. SH-SAW sensor

The SH-SAW sensor used is shown in Fig. 1. As the SH-SAW on the 36YX-$LiTaO_3$ has large electromechanical coupling coefficient, the crystal was chosen. For generating and receiving SH-SAW, a floating electrode unidirectional transducer (FEUDT) [16] was fabricated on the crystal. The FEUDT was adopted to reduce phase distortion and improve insertion loss [7]. The SH-SAW sensor consists of dual delay lines. The propagating surface of one delay line, channel (Ch.) 1, was metallized and electrically shorted by evaporated gold and titanium films. On the shorted surface, particle displacement only interacts with the adjacent liquid and then the SH-SAW is mechanically perturbed. The other delay line, Ch. 2, has a free surface area where the crystal surface is in direct contact with a liquid. As the electrostatic potential and particle displacement interact with a liquid, the electrical and mechanical perturbations are obtained. The electrical perturbation is detected by detecting differential signals between two delay lines. Center frequencies of the SH-SAW sensors used was 51.5 and 155 MHz. All sensors were obtained from Japan radio Co. Ltd. Design parameters of the SH-SAW sensor used is summarized in Table I. Figure 2 shows a liquid flow cell used.

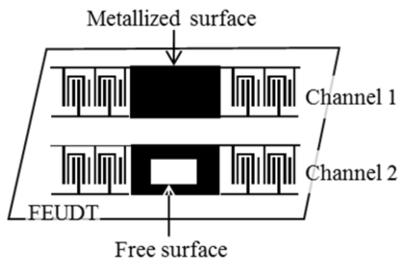


Figure 1. Schematic drawing of the SH-SAW sensor used.

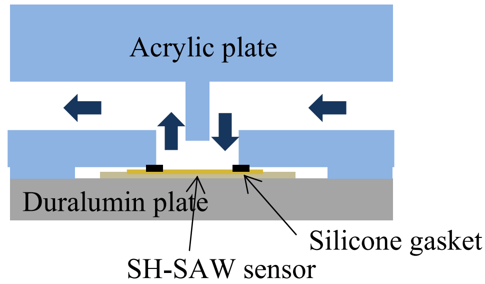


Figure 2. Cross section of the liquid flow cell.

TABLE I. DESIGN PARAMETERS OF THE SH-SAW SENSORS.

	51.5 MHz	155 MHz
Wavelength (λ)	80 μm	26 μm
Aperture	2,000 μm	666 μm
Number of pair	32	32
Distance between FEUDTs	11,000 μm	4,200 μm
Interaction length with liquid	4,000 μm 50 λ	3,000 μm 115.4 λ

B. Experimental setup

A sinusoidal signal from a signal generator (Anritsu MG3601A) is divided. One signal is directly connected to the vector voltmeter as a reference signal. The other is fed to the SH-SAW delay lines via a very high frequency (VHF) switching unit. The phase shift and amplitude ratio between the reference signal and Ch. 1 or Ch. 2 were monitored using a vector voltmeter (HP 8508A). The phase difference and amplitude ratio between the two channels was calculated using a PC. The velocity shift and normalized attenuation change were calculated from the phase difference and amplitude ratio, respectively.

Figure 3 shows the liquid flow measurement system with a peristaltic pump. Flow rate was fixed at 500 ml/min. A part of flow tube and a sample vessel were kept in a temperature-controlled chamber (ESPEC SU-240). The SH-SAW sensor with flow cell and pump were placed outside of the chamber. Temperature was varied from 10 to 80 °C. Temperature on the SH-SAW sensor was monitored using a thermocouple thermometer. The maximum temperature was determined on the basis of the actual DMFC.

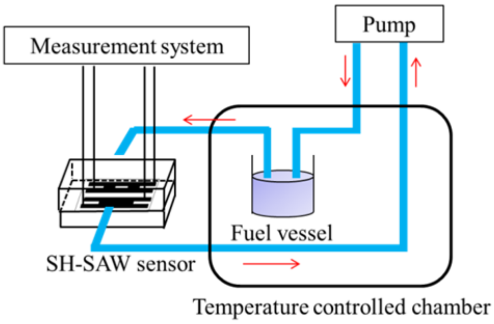


Figure 3. Experimental setup.

IV. RESULTS AND DISCUSSIONS

The MeOH solution of 3 wt% was measured. The concentration was decided on the based on the optimum concentration of a high-power DMFC. In Fig. 4, experimental results and calculated results of the velocity shift using eq. (5) are plotted. Reference temperature was 10 °C. When the temperature is lower than room temperature, the experimental results and theory agree well. However, the results from the 51.5 MHz SH-SAW sensor do not agree with the theory with increasing temperature. In eq. (5), conductivity of the sample is ignored. At high temperature, however, the conductivity cannot be disregarded. The conductivity depends on the temperature and it increases with temperature. In the equations, the conductivity is normalized by the angular frequency. This means that influence of conductivity reduces using a high frequency SH-SAW sensor. Therefore, reasonable results were obtained. We have proposed determination method of methanol concentration without any calibration [9]. The 51.5 MHz SH-SAW sensor was used. As the sensor responses and theory do not agree for the 51.5 MHz SH-SAW sensor, the electromechanical coupling coefficient was corrected. For the 155 MHz SH-SAW sensor, the correction of the electromechanical coupling coefficient is not necessary. The theory can be used to determine the MeOH concentration.

In Fig. 4, the ordinate is the velocity shift. The velocity shift is converted from measured phase shift. Here we compare the phase shift. The results are plotted in Fig. 5. Phase shift depends on the interaction length between the SH-SAW and liquid. The length is shown in Table. I. The converted length in wavelength of the 155 MHz SH-SAW sensor is longer than that to the 51.5 MHz SH-SAW sensor, reasonable results were obtained.

From Figs. 4 and 5, it is found that the best method to determine the concentration of MeOH solution is to use the high frequency SH-SAW sensor. The MeOH solution is liquid fuel for the DMFC. However, during electrode reaction, a formic acid is produced. The formic acid dissolves in the MeOH solution. In our previous research, we proposed the determination method of MeOH concentration of the binary-mixture solution of MeOH and formic acid using the 50 MHz SH-SAW sensor [6]. The

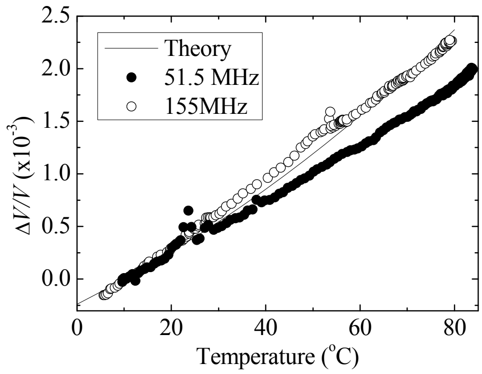


Figure 4. Comparison experimental results of 51.5 and 155 MHz SH-SAW sensors with the perturbation theory.

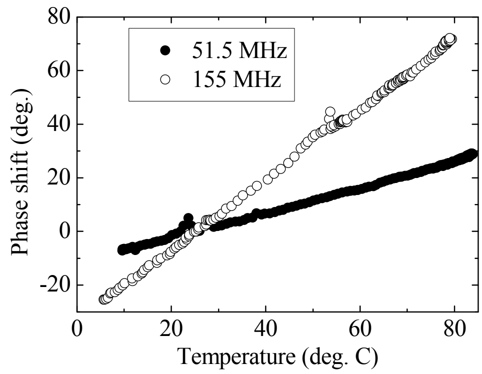
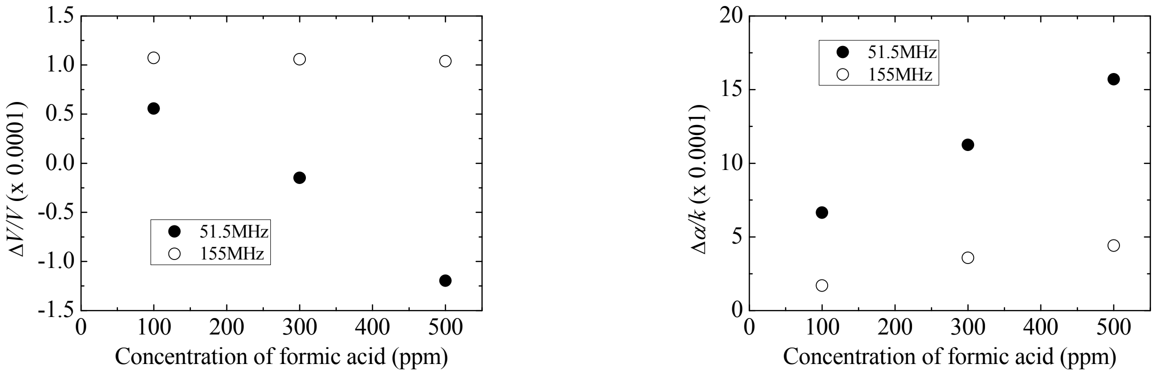


Figure 5. Phase shift as a function of the temperature.

method is complex and both velocity shift and normalized attenuation change are needed. If the MeOH concentration is determined from only the phase shift, a simple measurement system is realized and price will be decreased. Therefore, in this paper, the binary-mixture solutions of MeOH and formic acid were measured using the SH-SAW sensors and compared. The concentration of MeOH solution was fixed at 3 wt%. The value was decided actual value of the DMFC. Liquid was kept at room temperature. Figure 6 shows the velocity shift and normalized attenuation change as a function of concentration of formic acid. The velocity shift of the 155 MHz SH-SAW sensor is almost constant and the attenuation change is smaller than one of the 51.5 MHz SH-SAW sensor. The figure also exhibits that a high frequency SH-SAW sensor must be used to realize a MeOH sensor for the DMFC.

V. CONCLUSIONS

A MeOH sensor for a DMFC is required. In this paper, influences of the SH-SAW sensor for senor responses are experimentally and theoretically discussed. The MeOH solution can be assumed nonelectrolyte when the SH-SAW sensor frequency is high. From the results, the 155 MHz SH-SAW sensor is enough for this application. The advantage of using high frequency SH-SAW sensor is to reduce the influence of the conductivity. For the actual



(a) (b)

Figure 6. (a) Velocity shift and (b) normalized attenuation change as a function of formic acid conductivity in 3wt% MeOH solution.

DMFC, the formic acid is involved in the fuel solution. Obtained results in this paper suggest the means of the solving. Using the high frequency SH-SAW sensor, the MeOH concentration is determined from only the phase shift. Therefore, low price and simple measurement system will be realized using the high frequency SH-SAW sensor.

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