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Development of methanol sensor using a shear horizontal surface acoustic wave device for a direct methanol fuel cell

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Abstract

A methanol sensor for direct methanol fuel cell (DMFC) is required. A shear horizontal surface acoustic wave (SH-SAW) sensor for electrical property determination is applied for this purpose. The operating temperature of DMFC is above 50 °C. The wave propagation characteristics were calculated while considering temperature coefficient. The results indicate that the sensitivity increases with increasing temperature. Then, the concentrations of methanol solutions were measured using the SH-SAW sensor. Measured temperature ranged from 25 °C to 60 °C and concentration ranged from 0 to 50% by weight. Linear relationships between the sensor response and concentration were obtained. An increase in the sensitivity is experimentally confirmed. The limit of the detection was estimated from experimental results to be 0.1% by weight. Because formic acid is produced in the DMFC electrode reaction, its effect was discussed. The concentrations of mixture solutions of methanol and formic acid were measured. Using a chemometric method, we succeeded in determining the concentrations of both, simultaneously. Therefore, the SH-SAW sensor can be possibly used for DMFC.

Keywords: Shear horizontal surface acoustic wave sensor; Electrical perturbation; Direct methanol fuel cell; Methanol sensor; Estimation of methanol concentration in mixture solution

1. 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]. Because the SAW characteristics depend on an adjacent medium, a SAW device can be used as a sensor. If a liquid-phase SAW sensor is realized, a shear horizontal (SH) SAW must be used to avoid longitudinal wave radiation into the liquid [4,5]. The wave propagating on 36YX-$LiTaO_3$ is the SH-SAW [6], so this material has been utilized in liquid-phase sensors [7–10]. In previous research, we used the SH-SAW sensor for biosensor, liquid identification, and other applications. A unique feature of the SH-SAW sensor is its ability to detect liquid mechanical and electrical properties simultaneously.

The development of fuel cells has rapidly progressed due to environmental issues regarding global warming and the need for a substitute fuel for petroleum [11]. A direct methanol fuel cell (DMFC) is one of such cells, in which methanol is used as the raw material. A peculiarity of the DMFC is the possibility of miniaturization, so it can be used as a cell for mobile electronics, such as laptop PCs. As the efficiency of the DMFC depends on the concentration of methanol, a methanol sensor is required. We have measured the concentrations of alcohol solutions using the SH-SAW sensor [10]. The measurements were performed at room temperature. The results indicate that the SH-SAW detects the viscosity and dielectric constant of methanol solutions. On the basis of the results, the SH-SAW sensor can be used as the methanol sensor of DMFC. The working temperature of the DMFC, however, is normally higher than 50 °C. The material constants of liquids depend on temperature. It is important to know the influences of temperature on methanol detection.

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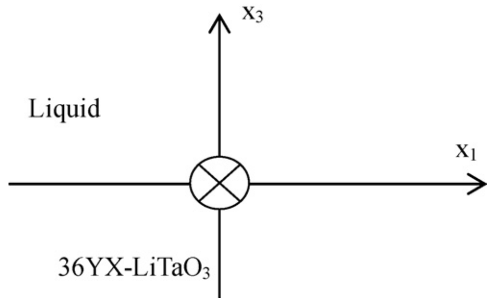

Fig. 1. Coordinate system used in this study. SH-SAW propagates in the x_1 direction.

In this paper, wave characteristics are calculated numerically [12,13]. The results suggest that the dielectric constant can be measured at high temperatures. Then, measurements using the SH-SAW sensor for determining electrical properties are performed. The SH-SAW sensor detects methanol solution with a high accuracy of 0.10% by weight. Moreover, a method of estimating methanol concentration in methanol and formic acid binary-mixture solution is proposed.

2. Numerical calculation

Numerical calculation method [8,10] is generally used to obtain the SH-SAW propagation characteristics. Numerical calculation method was proposed by Campbell and Jones [12]. Also, Yamanouchi and Shibayama proposed calculation method for a leaky SAW [13]. As the SH-SAW on 36YX-$LiTaO_3$ is the leaky SAW, Yamanouchi's method was used. However, Yamanouchi's method is for air/piezoelectric crystal structure. In this paper, we must consider influence of liquid. A solution for the structure of liquid/36YX-$LiTaO_3$ was reported by Moriizumi and Unno [7,14]. In this paper, we have used our original SAW calculation tool based on MATLAB®, which were programmed on the basis of those methods. Fig. 1 shows the coordinate system used in the present study. The SH-SAW propagates in the x_1 direction and attenuates in the $-x_3$ direction. The SH-SAW propagation surface was assumed to be electrically free or shorted. Kushibiki's material constant [15] was used for the $LiTaO_3$. For the temperature coefficients of $LiTaO_3$, we used Smith's value [16]. The material constants of a binary-mixture of methanol and water, such as viscosity, density, dielectric constant, were obtained from a chemical handbook [17].

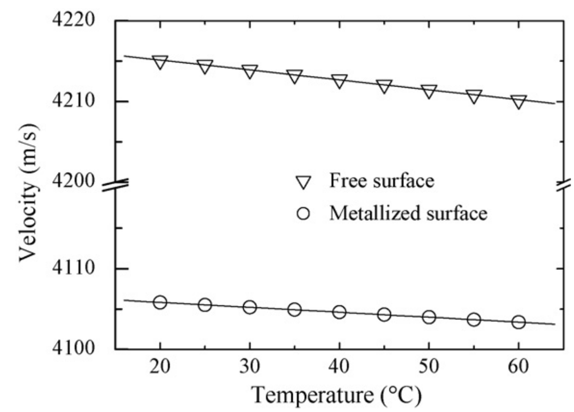

Fig. 3. Numerical calculation results of phase velocity as a function of temperature. The propagation surface is in contact with air.

Fig. 2(a) and (b) shows the calculated velocities for electrically free and shorted surfaces, respectively, with concentration as a parameter. When the liquid is loaded on the shorted surface, the SH displacement is affected. On the other hand, both SH displacement and static potential are influenced by the liquid, which is loaded on the free surface. For the free surface, the velocity increases with concentration and temperature. When the surface is shorted, the velocity decreases with increasing temperature. To discuss the difference in the changes of velocities, the velocities without the liquid were also calculated and results are shown in Fig. 3. The velocities for both surfaces decrease, as is well-known. In the case of Fig. 3, the velocity is only influenced by the temperature dependence of the crystal. If a liquid is loaded on the 36YX-$LiTaO_3$, it is necessary to consider influence of it. At constant temperature, velocity increases with decreasing a dielectric constant for the free surface and it increases with decreasing viscosity [8,9]. The dielectric constant and viscosity of methanol solution decrease with increasing temperature. Therefore, by comparing Fig. 2 with Fig. 3, we conclude the following: for the shorted surface, the temperature effects of the crystal are larger than those of the liquid. Therefore, the

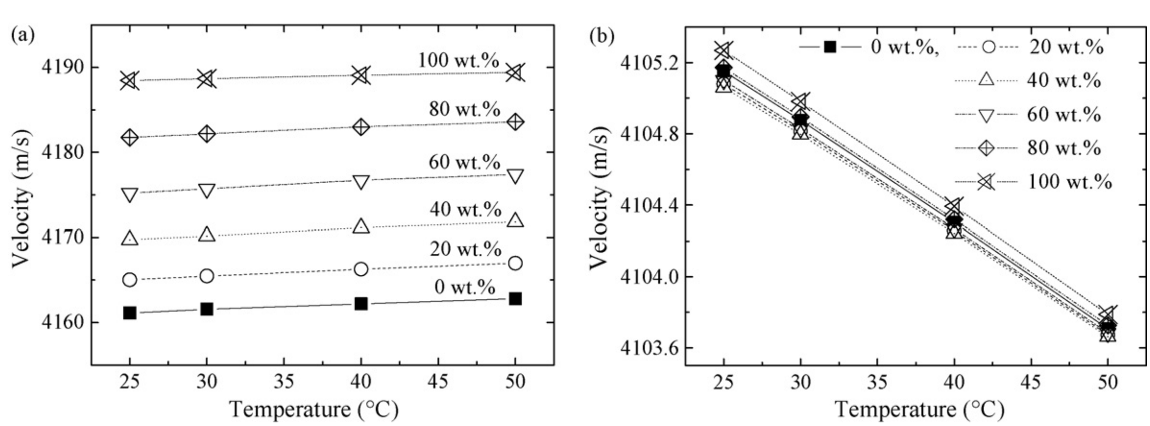

Fig. 2. Numerical calculation results of phase velocity as a function of temperature with methanol concentration as a parameter: (a) free surface and (b) shorted surface.

Table 1
Temperature dependence of the electromechanical coupling factor when water is loaded on free and metallized surfaces

25 °C	0.0269
30 °C	0.0272
40 °C	0.0278
50 °C	0.0284

calculated velocities decrease. For the free surface, as the temperature effects of the liquid are larger than those of the crystal, velocity increases. The results in Fig. 2 suggest that the velocity change for free surface is larger than that for the shorted surface. This means that the SH-SAW sensor for electrical property determination is desirable.

The approximate equations of the SH-SAW sensor for determining the electrical properties are represented as follows [9,10]. These equations were derived on the basis of the electrical perturbation:

$$\frac{\Delta V}{V} = -\frac{K_s^2}{2}\frac{(\sigma'/\omega)^2 + \varepsilon_0(\varepsilon_r' - \varepsilon_r)(\varepsilon_r'\varepsilon_0 + \varepsilon_P^T)}{(\sigma'/\omega)^2 + (\varepsilon_r'\varepsilon_0 + \varepsilon_P^T)^2} \tag{1}$$

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

where $\Delta V/V$ is the velocity shift, $\Delta\alpha/k$ the attenuation change, which is normalized by the wave number k, ω the angular frequency, ε_0 the dielectric constant of free space, ε_P^T the effective permittivity of the substrate, and ε_r and σ the relative permittivity and the conductivity of the liquid, respectively. The prime (′) denotes the sample liquid. K_s^2 is the electromechanical coupling coefficient and is derived from the following equation:

$$K_s^2 = \frac{2(V_0 - V_s)}{V_0} \tag{3}$$

Here, V_0 and V_s are the phase velocities when the reference liquid is loaded on the free and shorted surfaces, respectively. The velocity shift and attenuation change are proportional to K_s^2. As distilled water is used as the reference solution at the measurements, the effect of temperature on K_s^2 for the water is calculated from the numerical calculation results in Fig. 2 and summarized in Table 1. The coupling coefficient increases with temperature, so the sensor sensitivity for electrical property determination increases with temperature.

3. Experimental

A 36° rotated Y-cut X-propagating $LiTaO_3$ single crystal (36YX-$LiTaO_3$) was used as the SH-SAW substrate. Interdigital transducers (IDTs) and the sensing surface were designed and fabricated on the SH-SAW substrate using a conventional lithography. Fig. 4 shows the SH-SAW sensor for determining liquid electrical properties. The aperture of an interdigital transducer (IDT) is 2 mm, number of pairs is 32, and the center frequency is 50 MHz. The SH-SAW sensor consists of a dual SAW delay line. One of the SAW propagating surfaces is metallized and the other has a free surface area. When the liquid is loaded on

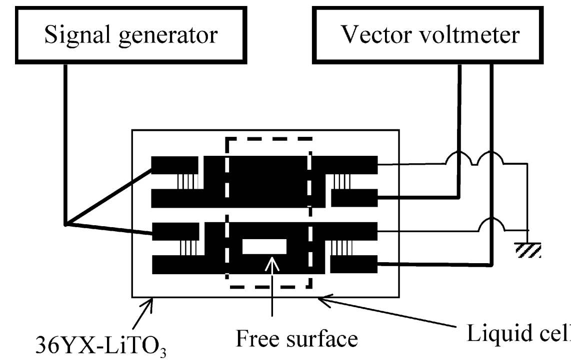

Fig. 4. Schematic illustration of the SH-SAW sensor for detecting liquid electrical properties with the signal generator and vector voltmeter.

the SH-SAW sensor surface, the SH-SAW on the shorted surface is mechanically perturbed and that on the free surface is mechanically and electrically perturbed. Therefore, by detecting differential signals between two surfaces, electrical perturbation is detected. Also, temperature effect decreases by detecting differential signal [18]. A 50 MHz signal from a signal generator (Anritsu MG3601A) was fed to the SH-SAW sensor. The outputs from the sensor were monitored by a vector voltmeter (HP 8508A). The phase difference and amplitude ratio between two channels were measured using the vector voltmeter. The phase shift, $\Delta V/V$, and attenuation change, $\Delta\alpha/k$, were derived from the phase shift and amplitude ratio, respectively.

A desktop high-temperature chamber (Espec ST-120) was used for temperature control. The SH-SAW sensor with a liquid cell was placed into the chamber. Temperature was varied from 25 °C to 60 °C. Temperature was measured using a thermocouple thermometer (Fluke 51K/J). In Fig. 5, the sensor head with the liquid cell in the chamber is illustrated. Also, methanol concentration was varied from 0 to 50% by weight. Distilled water at 25 °C was used as the reference solution.

4. Results and discussion

4.1. Measurement of concentration of methanol solution

Experimental results of the phase shift between reference water and samples are shown in Fig. 6. The lines in the figure are the best-fit lines. Linear relationships between concentration and phase shift are obtained. The slope and intercept of each line and correlation coefficient, R^2, are summarized in Table 2. The slope increases with temperature. In other words, the sensitivity of the

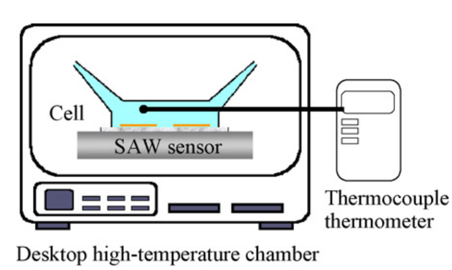

Fig. 5. Schematic illustration of the sensor head with the chamber. Liquid temperature is monitored using the thermocouple thermometer.

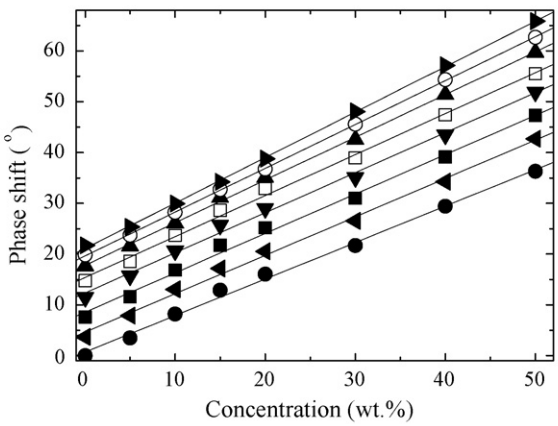

Fig. 6. Experimental results of methanol solution. Symbols shows the temperature, as follows: (●) 25 °C; (◄) 30 °C; (■) 35 °C; (▼) 40 °C; (□) 45 °C; (▲) 50 °C; (◯) 55 °C; (►) 60 °C.

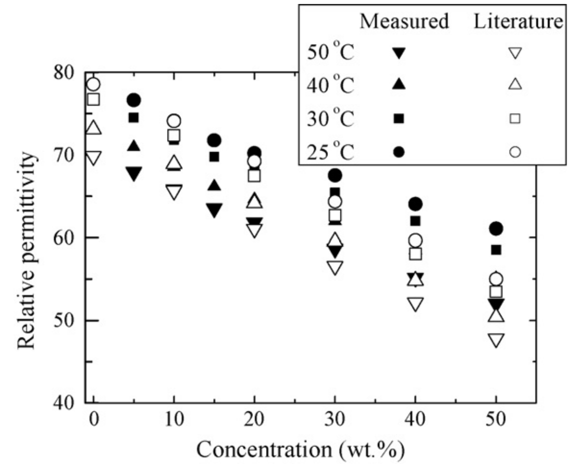

Fig. 7. Comparison of relative permittivity. Black symbols denote experimental values and white symbols denote literature values.

SH-SAW sensor increases with temperature. The results agree with the theoretical consideration as shown in Table 1. Also, high correlation coefficients are obtained. The concentration resolution was estimated on the basis of time stability. Concentration resolutions at 25 °C and 60 °C are 0.13 and 0.10% by weight, respectively. The optimum concentration of methanol is determined for a DMFC. The estimated concentration resolution is sufficient for practical purposes.

The relative permittivity of methanol was calculated using Eq. (1) and compared with the literature. The results are shown in Fig. 7. In the case of concentrations less than 20% by weight, the experimental values agree with the literature values. On the other hand, the experimental values do not agree when the concentration is higher than 30% by weight. These tendencies are commonly observed at each temperature. To clarify the reason, the propagating mode on 36YX-$LiTaO_3$ must be considered. The propagating wave on the shortened surface, which contacts with the air or the liquid, is SH-type pseudo-SAW. On the other hand, the wave propagating on free surface depends on the adjacent medium. When the surface contacts with low-relative-permittivity material, such as air, the propagating wave is a surface skimming bulk wave (SSBW) [19]. When the surface contacts with a high-relative-permittivity one, such as water, the SH-SAW propagates. Decreasing methanol concentration corresponds to a decrease in the relative permittivity, as shown in Fig. 5. Therefore, it is necessary to consider the influence of the SSBW. Eqs. (1) and (2), however, were derived without considering the SSBW. Fig. 7 indicates that effect of the SSBW cannot be disregarded, in the case of concentrations above 30% by weight. The best way to estimate the methanol concentration is to use the experimental equations as shown in Table 2.

Table 2
Slope and intercept of experimental equation in Fig. 4 and correlation coefficient

Temperature (°C)	Slope	Intercept	R^2
25	0.752	1.11	0.9957
30	0.771	3.72	0.9960
35	0.827	5.41	0.9950
40	0.899	6.42	0.9960
45	0.921	7.96	0.9966
50	0.942	9.41	0.9992
55	0.966	11.1	0.9988
60	0.988	13.2	0.9996

4.2. Measurement of concentrations of methanol and formic acid mixture solution

During electrode reactions in DMFC, hydrogen ions are generated from methanol [11]. During the process of the electrode reaction, formic acid is also generated [11]. As formic acid is mixed in the methanol solution, it is necessary to consider the method of methanol determining concentration in methanol–formic acid binary-mixture solution. The concentration of formic acid in solutions is known to be less than 0.1% by weight. Fig. 8 shows the measured results of the mixture solution. The concentration of methanol was fixed at 10% by weight. When formic acid is not involved in the solution, the methanol concentration can be determined from the phase shift, as shown in Fig. 6 and Table 2. For the mixture solution, however, the sensor responses become complicated, because the conductivity increases with the formic acid concentration. Phase shift and amplitude ratio decrease with increasing formic acid concentration. These results are reasonable and can be explained from Eqs. (1) and (2) by substituting permittivity and conductivity. From Fig. 8, the sensor responses for formic acid of 0.1% by weight saturate when temperature is higher than 50 °C. The results indicate that the estimation of methanol concentration at high formic acid concentration is difficult.

To consider the method of determining the methanol concentration, $\Delta V/V$ and $\Delta\alpha/k$ are derived from phase shift and amplitude change, respectively. The obtained values are plotted on the $(\Delta V/V)$–$(\Delta\alpha/k)$ plane, as shown in Fig. 9. The plotted data were measured at room temperature. The dots denote the experimental data. M and F in the figure represent methanol and formic acid, respectively. The numbers indicate the concentration. For example, M5 is 5% methanol by weight and M10 + F0.1 is the mixture solution of 10% methanol and 0.1% formic acid. Straight lines in the figure are used to connect points. Now we

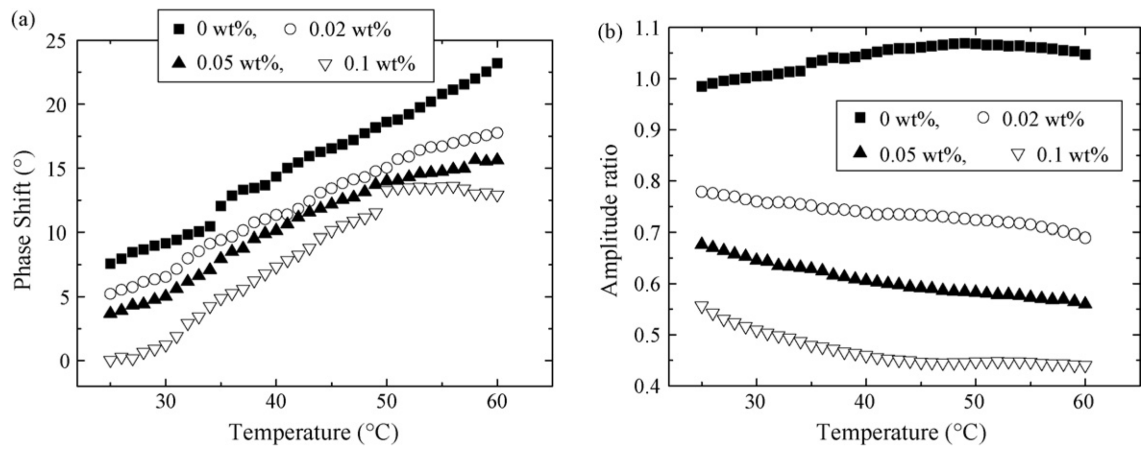

Fig. 8. Experimental results of methanol and formic acid binary-mixture solution. (a) Phase shift and (b) amplitude ratio. Methanol concentration is fixed at 10% by weight and formic acid concentration is a parameter.

consider the quadrilateral ABCD. Segments AD and AB indicate the concentrations of methanol (0–5%) and formic acid (0–0.02%), respectively. The measured data on $(\Delta V/V)$–$(\Delta\alpha/k)$ plane performed the coordinate formation to AD–AB plane, and the concentrations were estimated using the following equations:

$$x = 21014\left(\frac{\Delta V}{V}\right) + 3543\left(\frac{\Delta\alpha}{k}\right) \quad (4)$$

$$y = -1.683\left(\frac{\Delta V}{V}\right) + 17.52\left(\frac{\Delta\alpha}{k}\right) \quad (5)$$

where x and y are the concentrations of methanol and formic acid, respectively. For example, the experimental result of the unknown concentration is located at the point (X) denoted by a triangle in the figure. The results of velocity shift and attenuation change were substituted into Eqs. (4) and (5). The estimated results are 3.9% methanol by weight and 0.009% formic acid by weight.

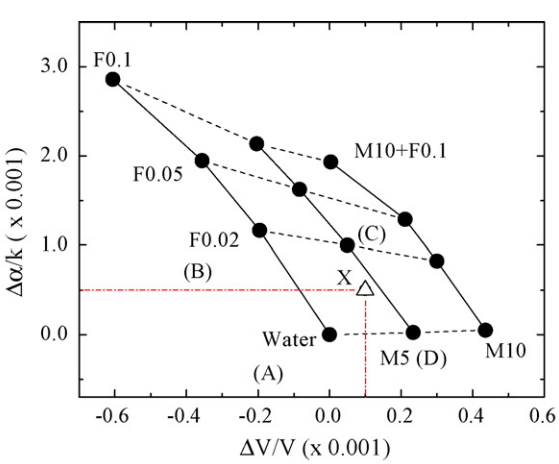

Fig. 9. Evaluation of methanol and formic acid binary-mixture solutions. Black circles: experimental results; X (triangle): unknown sample. M and F denote methanol and formic acid, respectively. The numbers indicate the concentration of the solution.

5. Conclusions

In this paper, we described the SH-SAW sensor for use as a methanol sensor of DMFC. Numerical calculation results indicated that the determination of dielectric constant is well suited for this application and the sensitivity increases with temperature. The increase in the sensitivity was confirmed by the experiments. Also, the resolution was derived from the experimental results to be 0.10% by weight at 60 °C. Therefore, the SH-SAW sensor is suited for use as a methanol sensor for DMFC. Moreover, the influence of formic acid was considered. A method of estimating methanol concentration in methanol and formic acid mixture solution was examined. A simple and effective method was proposed. In future, influence of other by-products, such as formaldehyde and carbonic acid, must be considered. Also, developing a SH-SAW sensing system for DMFC is future work.

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Biographies

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