

## Sensor Platform for Measuring the Concentration in Aqueous Solutions by Cyclic Voltammetry and Impedance Spectroscopy

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**Abstract**— This article describes sensors for concentration measurement based on the electro-chemical properties of the liquid being measured. Herein two electrical methods, namely cyclic voltammetry and impedance spectroscopy, are being presented. The measurement can be performed quasi simultaneously using the same measurement medium. Further optimization of the combined methods are possible by adapting the geometric design of the electrode structure, the electrode material, the optional passivation and the electric coupling (galvanically or capacitively). In summary, by combining multiple sensory principles on a device it becomes possible to analyze mixtures of substances contained in a solution with respect to their composition.

**Keywords;** *interdigital structure; impedance spectroscopy; cyclic voltammetry; silicon.*

### I. INTRODUCTION

Sensors for concentration measurements are a very vast area of research. A concentration measurement is used when the components are known, but not their content. For their determination several substance-specific sensor principles are known. In this article, two electrical methods are presented using the implementation as the sensing element is reported. These methods are based on cyclic voltammetry and impedance spectroscopy. In cyclic voltammetry a rising and then sloping current is applied between the working electrode and the counter electrode in a solution. The potential is determined by a reference electrode. If there is a redox-active substance in the solution, it will be oxidized or reduced at a characteristic potential. The current is recorded as a function of voltage. The voltage in the oxidation and reduction and the corresponding maximum current are of interest. Impedance spectroscopy detects both the dielectric properties of a medium and its conductivity as a function of frequency. In aqueous solution, these properties are dependent on the concentration.

The base of the sensors is an interdigital structure. Figure 1 shows different variations of designs. The main features can be combined freely. A galvanic or capacitive coupling is possible. The DUT can be a liquid or a solid. The organic or inorganic sensitive solid is applied directly to the sensor surface. The thickness is only a few 100 nm and is micro- or nano-porous. This binds substances (DUT) by absorption from the surrounding atmosphere, such as water or carbon dioxide. The electrical properties change due to this and are determined by the spectroscopy. Table 1 shows the different materials for the sensor.

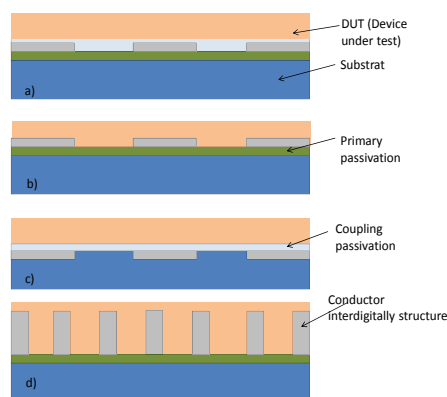


Figure 1. Various design options a) interdigital structure, passivated for a capacitive coupling, b) interdigitated structure without passivation, galvanic coupling, c) implanted in silicon interdigital structure, d) 3D interdigital structure

TABLE 1. OPTIONAL MATERIALS FOR THE SENSOR

Base material	Silicon, (optional) Borosilica
Passivation Base material	SiO <sub>2</sub>
Conductor	Doped Silicon, MoSi, Gold Platinum
Passivation Conductor (optional)	Si <sub>3</sub> N <sub>4</sub> , ZrO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> (20 nm to 500 nm)

In addition to the measurement of purely chemical parameters, such as concentration, measurement of biological media is possible. The evaluation of the measurement results, however, requires great experience. In [1] and [2], the dielectric measurement of a biological medium is described by some examples.

Often the signal is not very selective on the type of material. In the DUT (device under test) the selectivity of the sensor can be increased adding an indicator; using the mixing ratio and the associated change in impedance even a multi-component system can be analyzed. Further optimization of the combined methods are possible by the geometric design of the electrode structure, the electrode material, the optional passivation and the electric coupling.

The combination of multiple sensory principles on a device can be used to analyze a multicomponent system with a simple sensor.

Section II represents the principle for the combined impedance spectroscopy and cyclic voltammetry, the base of the sensor platform, the various of this and the electronic circuit. Section III represents the measurements for the evaluation and calibration of the sensor various. Section IV shows a sample application. Section V concludes the article.

II. EXPERIMENTAL SETUP

For the evaluation and adaptation of the sensor's design, a test setup was constructed. The design is configured such that the distances can be selected in a range of 200 microns with free a resolution of 5 microns. In Figure 2, the measuring principle is shown. By choosing the connections of the electrode gap can be selected. In [1] and [2], this method is described in detail.

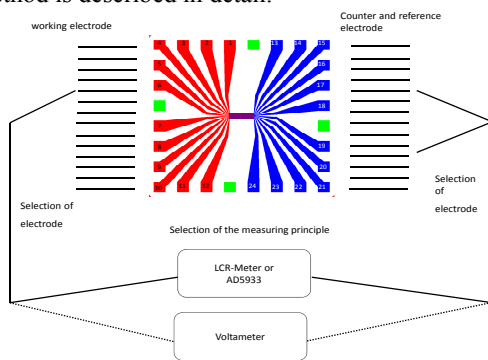


Figure 2. The principle for the combined impedance spectroscopy and cyclic voltammetry

The measurement setup for impedance spectroscopy can be seen in Figure 3. Here, the analysis-chip with the interdigital structure on it is seen in the middle. It is surrounded by 12 dual multiplexer, which can be used to select the 24 measurement channels (12 per page). On the left side of the figure there are SMA connectors for connecting an external LCR meter to chip, with which the impedance of the device can be measured.

Through the recess in the middle, the liquid which is to be investigated can be applied to the interdigital structure either directly, or a flow chamber can be installed to then perform the impedance spectroscopy using the desired channels.

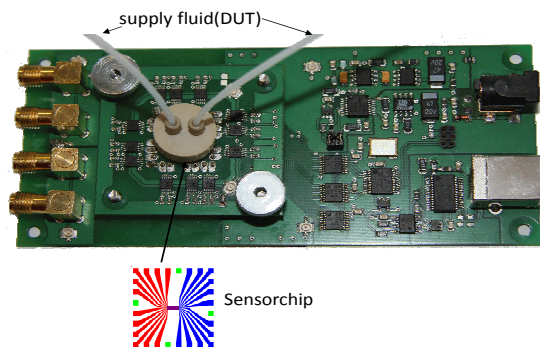


Figure 3. The electronic circuit for the combined impedance spectroscopy and cyclic voltammetry with die connector for the fluid

Figure 4 shows the sensor for the combined impedance spectroscopy and cyclic voltammetry. With the aid of a multiplexer array, a line-bound connection between the measuring object and the impedance spectrometer is established. Subsequently, the impedance spectroscopy is performed for the selected channel.

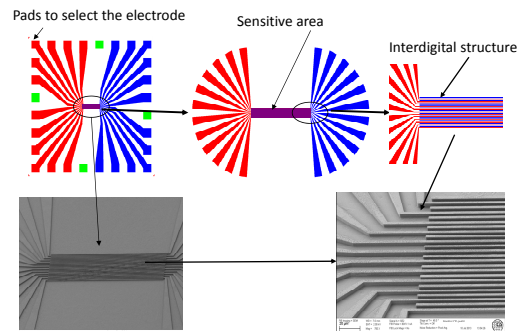


Figure 4. The sensor for the combined impedance spectroscopy and cyclic voltammetry

III. MEASUREMENTS FOR EVALUATION

For the evaluation and calibration of the sensor measurements are performed on an aqueous solution of KCl, ranging from 0.00002 mol/l to 1 mol/l. Figure 5 shows the frequency dependent measurement of the impedance  $|Z|$  of the aqueous KCl solution, the distance between the electrodes is constant.

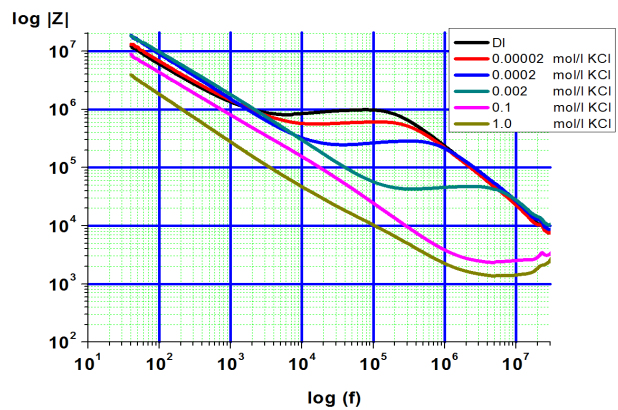


Figure 5. Concentration measurement, variation in the concentration

In Figure 6 the result when measurement is being performed at different distances of the electrodes is shown. In this way, the appropriate geometric structure is found for the measuring task.

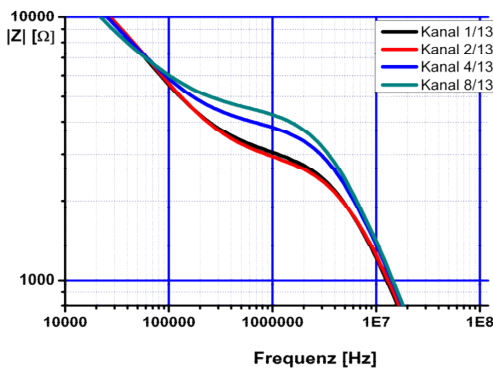


Figure 6. Concentration measurement, variation of the electrode distance

With the aid of the measured values, the amount and phase  $|Z|$ , an equivalent circuit diagram is developed. The values for the components are determined by a curve fitting. The results are shown in the Figure 7. The equivalent circuit is now allowing for the calculation of the resistor R1 from the measured values and the calibration of the sensor to the conductance. Figure 8 shows the graph of the curve fitting.

Parameters	Upper Limit	Lower Limit	Result In.Val.	Error %	Fix
C1	6.7785e-13	6.7785e-13	6.7785E-13	1.016	<input checked="" type="checkbox"/>
R1	1000000	0	2.4802E05	3.7676	<input type="checkbox"/>
P1	0.0005	0	5.2288E-10	3.7702	<input type="checkbox"/>
n1	1	0	0.83005	0.51933	<input type="checkbox"/>

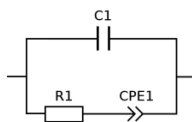


Figure 7. Equivalent circuit diagram and the curve fitting

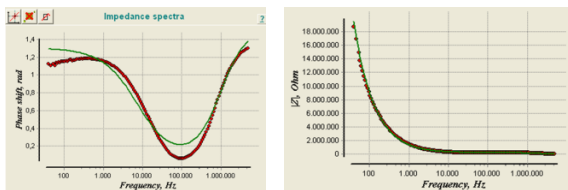


Figure 8. Graph of the curve fitting

In Figure 9 the resistances as a function of concentration from the curve fitting are plotted. Various layer structures, geometries and measurement strategies are explored. The aim is to explore a multi-component system with various sensors at the same location. The concentration of the components is derived from the signal pattern. If the sensor is calibrated, the concentration of the ingredients can be determined from the signal pattern. One application is the in-line measurement in biogas plants to optimize the output.

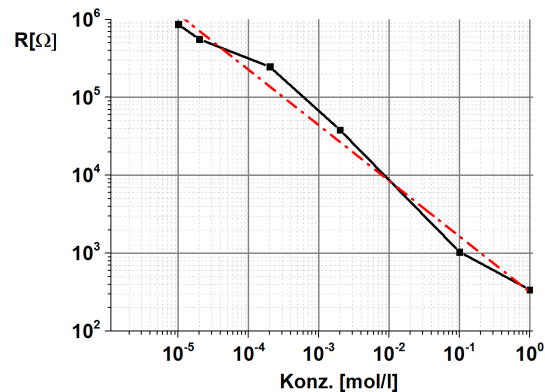


Figure 9. Concentration measurement, variation of the electrode distance

An overview of the previous work done is detailed in [3]-[5]. The cyclic voltammetry is partially used in micro-sensors, but not in combination with the impedance spectroscopy. The essential idea and novelty are related to the connection of several measurement principles and sensitivities to determine the concentration at the same location. In summary, by combining multiple sensory principles on a device it becomes possible to determine the composition of substances contained in solution.

#### IV. EXPERIMENTS ON THE TERNARY SYSTEM WATER-ACETIC ACID-PROPIONIC ACID

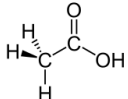
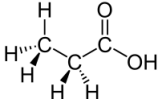
The ratio of acetic acid-propionic acid is a control parameter for the operation of biogas plants [6]. The sequence of processes in biogas plants is not explained here, an intrigued reader might take a look at [7]. The concentration measurement in this mixture is very challenging because acetic acid and propionic acid share similar chemical properties. The separate determination of the concentration of acetic acid and propionic acid in the mixture of the two materials is difficult because both materials differ structurally only by an additional-CH<sub>2</sub>-group, which is insignificant in terms of responsiveness and many physical properties

Cyclic voltammetry is preferably used to investigate redox processes in terms of their mechanism. It turns the electrode material used as a limit to the administrable voltage. Since acetic and propionic acid can be reduced only under very drastic conditions to the aldehyde, it can be expected that the cyclic voltammetry for the quantitative determination of these two components provides no useful results.

For the same reason, actually, no significant differences in the dielectric properties of both substances in the impedance spectroscopy arise. A variety of electrochemical processes are modeled in the equivalent circuit with a CPE (constant phase element). This reflects the ion mobility in the solution, which also depends on the mass of the moving particle. Thus the different molar masses of acetic and propionic-acid could be used for the analysis in this way. In Table 2, the two substances are shown.

R1 and C3 in this case represent the influence of the used multiplexer on the recorded spectra, while the remaining elements result from the properties of the comb structure used and of the measured liquid. First results show the practicability of this method. In addition, by varying the electrode spacing, all the other parameters which are characteristic of the liquid can be varied in order to eliminate them by a subsequent subtraction.

TABLE 2. COMPARISON OF ACETIC ACID AND PROPIONIC ACID

	acetic acid	propionic acid
		
Molmass (g mol <sup>-1</sup> )	60,05	74,08
pK <sub>s</sub>	4,76	4,87
Refractive index	1,371	1,386

### V. CONCLUSION SECTION

With the sensor platform described in the article could be shown that a combination by cyclic voltammetrie and impedance spectroscopy in a measuring system is possible and above all useful. Furthermore it could be shown by the various sensor adjustments (geometry, material, etc.) of the sensors used, and that this increased sensitivity liquids can be analyzed optimal. These optimizations are thus of crucial importance and represent an important decision process for the application areas of the sensor platform. These improvements will also enforce the ability to distinguish between liquids in a liquid mixture. For the sample application in Section IV, this means: To optimize the sensor, the geometrical layout will be modified increasing the sensitivity to discriminate better between acetic acid and propionic acid.

### ACKNOWLEDGMENT

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