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HTCC multilayer based on sensitive sensors for water analysis

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Summary:
Based on a microsystem technology approach, electrochemical sensors for analysis of H^+, NH_4^+, K^+, Ca^{2+} and Cu^{2+} ion concentrations were developed. Starting from a suitable material and process development ion-sensitive thick-film membranes were deposited on a ceramic HTCC multilayer sensor platform. All ion-sensitive electrodes ISEs have a very good response behavior and high sensitivity in the examined measuring range. Thus the ceramic multilayer technology provides as a suitable method to prepare robust and miniaturized multi-sensor for water analysis.

Keywords: Ion-sensitive electrodes, ceramic multilayer technology, thick-film technology

Motivation

Monitoring water quality is essential to protect the environment and health. In the areas of drinking water and wastewater monitoring, intelligent agriculture, food industry, etc., the determination of different ion concentrations is necessary. Users place increasing demands on the sensors with regard to their measuring properties, robustness, miniaturization, geometry variability and manufacturing costs. The sensor requirements are particularly aimed at functional integration and smart, cheap, miniaturized multisensors for mass applications. According to the state of the art usually potentiometric sensors for ion concentration measurements, so-called ion-selective electrodes (ISEs) are used. These ISEs are based on various, mostly precision mechanical manufacturing technologies. Their manufacture is quite expensive and the miniaturization potential is limited. The aim was therefore to overcome these restrictions and to use technologies of ceramic multilayer technology in order to produce cost-effective and miniaturized multi-sensors for water analysis.

Approach

Components made of ceramic multilayer technology have conquered broad areas of application in various areas of electronics and microsystem technology. A ceramic multilayer is an intelligent ceramic packaging, which is produced by 3D structuring and material integration. By the excellent three-dimensional structuring and functionalization of ceramic, robust sensor solutions for the 3D packaging technology of sensory microsystems are realized. With sensor miniaturization, the ceramic multilayer technology also offers an economical aspect of sensor production. The aim of the development work was therefore to use the **H**igh **T**emperature **C**ofired **C**eramics (HTCC) multilayer technology to implement a ceramic-based integration platform for various ion-sensitive sensors, which can be used in numerous analytical and industrial processes for water analysis.

Results

Using the ceramic HTCC film and multilayer technology, a platform for the integration of electrochemical sensors for water analysis has been developed. The green foils are structured using micromachining processes such as punching, lasering or embossing. Depending on the version (see Fig. 1), sensor arrays of different layouts can be manufactured on top. The individual sensitive layers are obtained by depositing special functional layers on the ceramic using screen printing. The sensitive layers are interchangeable on the sensor array depending on the application. In the presented example, the functional proof for the determination of the measured values pH, Cu^{2+} heavy metal ion as well as the cations Ca^{2+}, NH_4^+ and K^+ in aqueous solutions was provided. The main challenge was the material and process development for the deposition of ion-sensitive thick-film membranes on the ceramic sensor platform. For that the functional materials are processed into powders of small grain size, which are dispersed in an organic binder. The paste is subsequently processed on a three-roll mill in

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order to obtain a homogeneous, screen-printable suspension. The firing or curing of the functional layers is carried out according to their sintering properties. A thick film reference electrode is integrated on bottom.

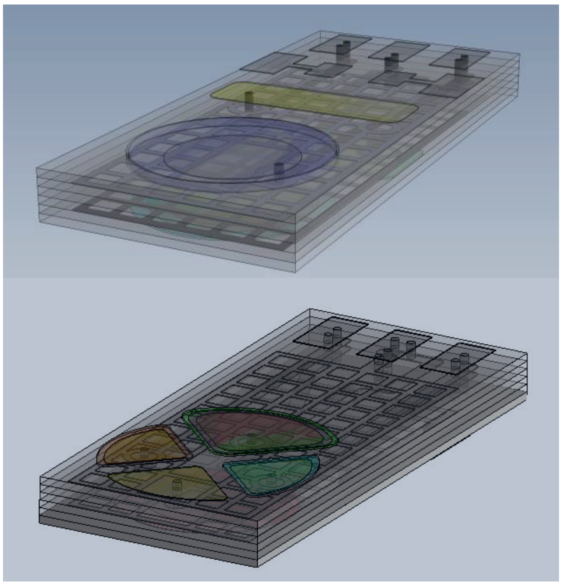

Fig. 1. HTCC sensor platform with two different layouts

The ISEs are potentiometric indicator electrodes that respond to the activity of the type of ion to be determined. Here, potentiometry, as an electro-analytical method of quantitative analysis, uses the concentration dependence of the electrochemical potential. The potentials were measured with a Keithley electrometer at 25 ° C.

Mini pH sensor

For the pH-sensitive glass layer, a SiO_2-Na_2O-MgO-MnO_2 glass is used that sintered at 640 ° C. In order to obtain dense, crack-free glass layers, the coefficient of the thermal expansion of the glass must be matched to that of the HTCC ceramic. The sensor is manufactured on a tile in 55-fold use (see Fig. 2).

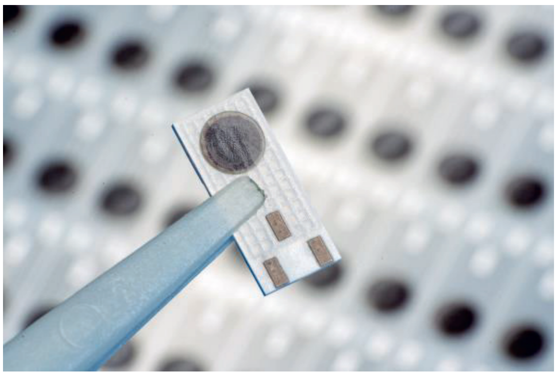

Fig. 2. Mini pH sensor

The slope of the measuring chain in the measurement range from 1.68 pH to 9.18 pH is in good agreement with the Nernst equation for monovalent ions.

Cu^{2+} ISE

In accordance with the thermochemical, crystallization and sintering behavior of the copper chalcogenide glasses, the thick-film pastes made from the glasses were processed in such a way that thin glass membranes were deposited on the HTCC multilayer, which are copper ion sensitive. The sensitivity of a CuAgAsSe thick film electrode is in the measuring range from 10^{-2} M to 10^{-6} M $Cu(NO_3)_2$ solution at 27.3 mV / pCu^{2+}. This value corresponds to Nernst's behavior for divalent ions and correlates very well with the sensitivity of the bulk material (see Fig. 3).

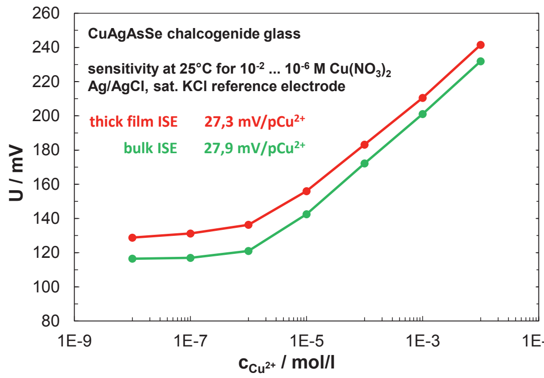

Fig. 3. Characteristic curve of Cu^{2+} ISE in measurement range 10^{-2}…10^{-8} M $Cu(NO_3)_2$

K^+, NH_4^+, Ca^{2+}

The polymer-based, ion-sensitive membranes of the K^+, NH_4^+ and Ca^{2+} ISEs are screen-printed and cured at room temperature. All ISEs have a very good response and high sensitivity in the studied measuring range in good agreement with the Nernst equation (see Fig. 4).

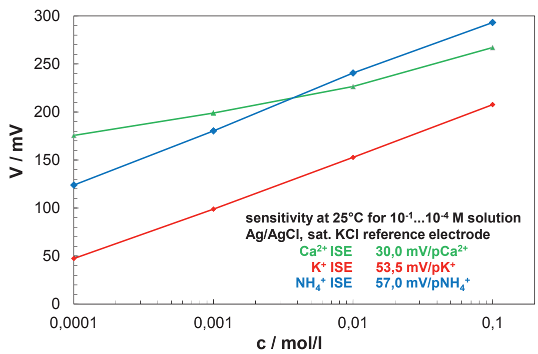

Fig. 4. Characteristic curves of ISEs (K^+, NH_4^+, Ca^{2+}) in measurement range 10^{-1}…10^{-4} M solution