

# Preparation and Measurement of Combinatorial Screen Printed Libraries for the Electrochemical Analysis of Liquids

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A combinatorial approach to the development of new screen printing pastes is introduced. We used a novel technique for printing electrodes out of different binary mixtures of pastes. The pastes applied are based on the transition metals iridium and ruthenium in the form of their (IV) oxides. Using multielectrode arrays, these pastes were printed on the same substrate in one single step. In this work, pH sensors were printed based on a concept using solid state electrodes both with the measurement and the reference electrode. After the sintering process, the pastes were then evaluated using a robotic setup designed to handle the high impedances characteristic for pH sensors as well as to automatically manipulate the fluids in contact with the sensors.

## Introduction

Screen printing is one of industry's most important and powerful structuring techniques for the manufacturing of sensors as well as circuit interconnects or functional units, which need to be manufactured in a fast and easily scalable way.<sup>1</sup> Its original development took place in the printing industry, and it is there mainly used to manufacture large billboards or banners.<sup>2</sup> Screen printing is an especially interesting preparation method for sensors to be applied for the testing of gases and liquids, which are made out of functionally active materials that have to be incorporated into a printable paste. In this work, iridium(IV) oxide and ruthenium(IV) oxide are used to prepare a paste that can be used to manufacture pH sensitive electrodes. In the past, screen printing has been used extensively in combinatorial chemistry but only to provide e.g. electrical contacts to combinatorially varied sensor materials or as a base material, which is then coated with a variety of other elements.<sup>3</sup> Yet the combinatorial approach has not been used to develop printing pastes themselves. Testing the different recipes and materials for the preparation of the printing pastes opens up a wide parameter space. A rapid and automated way of evaluating the samples represents a challenge. In this work, we present a novel technique for printing and measuring screen printing pastes. Different materials can be printed in one single step, measuring of these materials is performed with the use of a robotic device. It is designed to handle the high impedances that occur at pH measurements and is also

able to manipulate the liquids in contact with the different sensor materials.

## Preparation of the Screen Printing Paste

The active material that is supposed to be printed (e.g., silver for conductor pathways or zirconium oxide for oxygen sensors in automotive exhaust gas systems) is milled down to a fine powder.

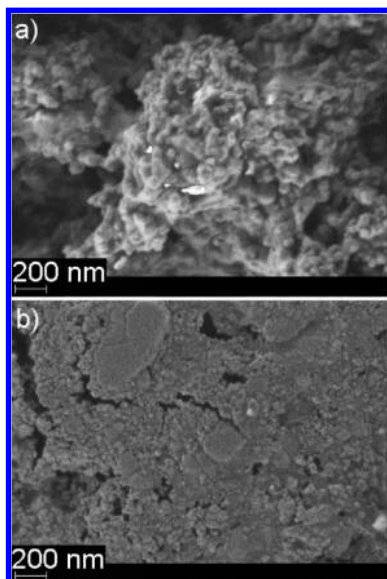
A part of the powder usually also consists of the finely milled particles of the substrate material to ensure better sintering properties of the paste during and after the sintering process. The content of the added ceramic has to be chosen in a way that ensures the formation of one single phase during the sintering process without hindering the formation of percolation paths in the printed structures. This combination of active material and ceramic powder is then mixed with appropriate organic base oil. Such base oils typically consist of up to ten different organic compounds, covering the whole range from simple aliphates to complex aromatic molecules. The base oils in this work consisted of glycole ethers, polyvinyl butyral, phthalates, and secondary alcohols in the ratio 7:2:1:10. The respective composition which was applied for each individual material was empirically found and optimized for each individual material and lot with respect to the processability. The base oil in combination with the respective mass amount of the milled down powder governs the behavior of the screen printing paste. It must not be too viscous, otherwise the paste will not pass properly through the mesh. It must not be too fluid, otherwise the printed structures will have fringes and flow together at the edges. The organic substances must not evaporate too fast, otherwise the paste will be too sticky and not be printable after a short amount of time in contact with air, yet they have to evaporate fast enough to ensure well defined structures once the paste is printed. After the thorough homogenization of base oil, active material, and ceramic

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**Figure 1.** (a) SEM image of the surface of screen printed iridium(IV) oxide. (b) SEM image of the surface of screen printed ruthenium(IV) oxide.

powder, the mixture is heated up to 80 °C for typically 5 to 10 min to achieve the wanted viscosity by evaporating parts of the organic substances. The pastes prepared this way are stored at 8 °C in a sealed container to hinder evaporation of the remaining organics.

### Materials

A pH electrode based on a potentiometric principle consists of two electrodes. One is the measuring electrode. At its surface, an electric double layer is formed when in contact with a liquid. The potential over this double layer changes with pH in the medium. Iridium(IV) oxide and ruthenium(IV) oxide are materials that have been identified in a previous work to be pH responsive.<sup>4</sup> Screen printed iridium(IV) oxide electrodes have been manufactured,<sup>5</sup> as well as ruthenium(IV) oxide ones.<sup>6</sup> The other electrode is the reference electrode. Its surface potential is not affected by a pH change in the liquid. A silver/silver chloride electrode is commonly used as a solid state electrode to serve this purpose.<sup>6</sup> Measuring therefore the potential between these two electrodes allows to determine the concentration of acid in a given medium. The theoretical potential value  $V$  of the electrode is given by the Nernst equation  $V = -59.2 \text{ mV} \times \text{pH}$ .<sup>7</sup>

The measuring electrodes were screen printed on low temperature cofired ceramics.<sup>8</sup> All materials used were reagent grade. Iridium(IV) oxide powder and ruthenium(IV) oxide powder were obtained from Alfa Aesar, LTCC substrates and powder, from Sumitomo. Figure 1 presents scanning electron microscopy (SEM) images of the surfaces of the screen printed electrodes. The grain size of iridium(IV) oxide a) is approximately 50 nm. Spongelike structures are characteristic for this surface, enlarging its area furthermore. In contrast to that, the surface of the ruthenium(IV) oxide in Figure 1b appears flat and less porous. The grain size is smaller, approximately 10 nm.

The reference electrode was prepared in a similar way. A silver screen printing paste by Robert Bosch GmbH was used

to prepare the electrodes. After the sintering process, the silver electrode was anodized using a 5 wt % solution of potassium chloride by Merck in deionized water. A current of 100  $\mu\text{A}$  was applied for 90 s.

Figure 2 shows SEM images of the surface of the screen printed silver reference electrode before (a) and after the ionization (b). The energy dispersive X-ray (EDX) analysis of a chlorinated silver surface is shown in part c. Silver and chlorine are detectable.

A screen printed sensor with an interdigital design is shown in Figure 3. The dark measuring electrode is lying below with the silver reference electrode above. The prepared sensors were then tested in water to check their behavior with a varying pH value. The potential between the measuring and the reference electrode was obtained by a pH meter. A conventional pH glass electrode was used to cross check the performance of the screen printed sensors.

Figure 4a shows the measured potential between a ruthenium(IV) oxide and silver/silver chloride electrode in deionized water while the pH is changed by adding acetic acid. Although a reaction to a falling pH is visible, the reaction is quite slow as it takes several minutes until a stable potential is reached at pH values  $< 3$ . A faster reaction is shown in Figure 4b. The iridium(IV) oxide sensor reacts within several seconds. After the pH reaction of both sensor systems has been shown, it is now of interest what a combination of both measuring electrode materials might yield.

### Preparation Method

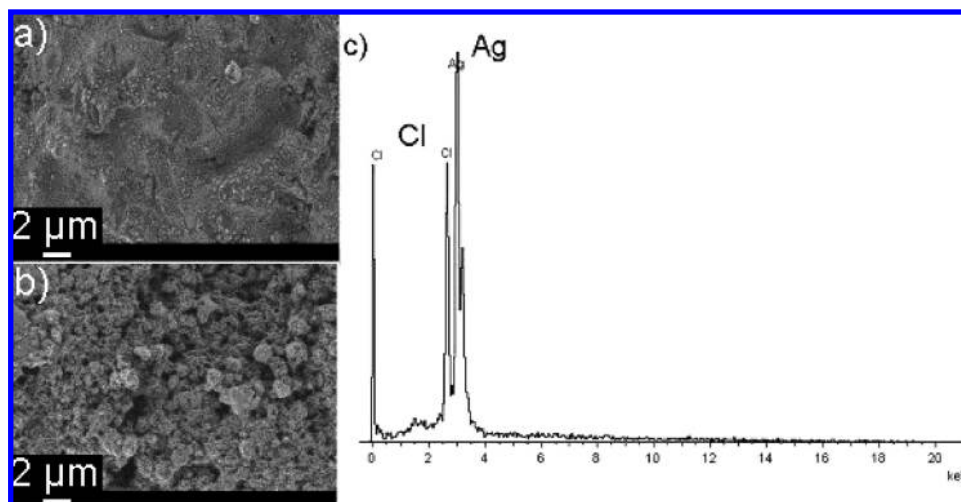
Screen printing is a one material at a time process. The screen and the rubber squeegee that presses the paste through the screen have to be cleaned, and the substrate has to be aligned if there are several screen printing steps to make sure that the structures are adjusted properly. After the printing, the cleaning and alignment process must be repeated. To speed up this process and to make it possible to print several different materials in one single printing step, the following technique was introduced.

Elastic barriers were affixed to the printing screen (Figure 5), separating longitudinal parts. These parts are then filled with different printing pastes. A squeegee with gaps at the location of the elastic barriers is drawn over the screen, pressing down the screen at the paste coated parts. The advantage of this process is that whereas in the past, every change of paste needed one printing process with the need for cleaning the machine and readjusting the substrate, now several different materials can be printed in one single step.

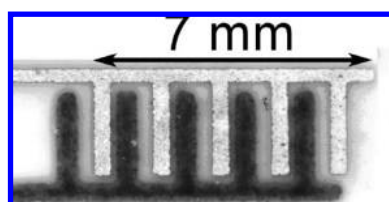
A substrate prepared in this manner is shown in Figure 6. Ruthenium(IV) oxide and iridium(IV) oxide pastes are mixed as shown by the ratios. The paste mixtures were produced on the gram scale and the ratio between the ruthenium(IV) oxide and iridium(IV) oxide pastes were determined gravimetrically. Other ruthenium(IV) oxide and iridium(IV) oxide pastes in a pure composition but with different organic content (RuO<sub>2</sub> b, IrO<sub>2</sub> b, IrO<sub>2</sub> c) were also printed (b 40% glycole ethers, c 45% glycole ethers).

### Measurement Method

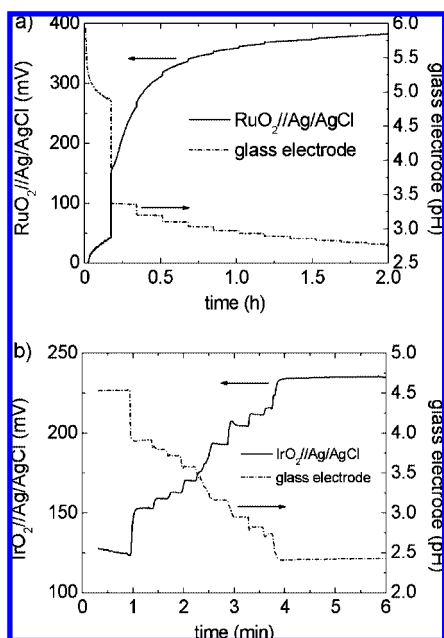
There is a multitude of approaches to measuring combinatorial libraries. A quasi parallel concept for measuring 64



**Figure 2.** (a) Surface of a screen printed silver reference electrode. (b) Same surface after anodization in a potassium chloride solution. (c) EDX analysis of a chlorinated silver electrode. Only silver and chlorine are detectable.



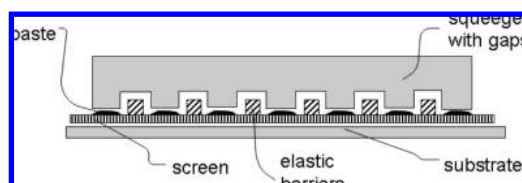
**Figure 3.** Screen printed pH sensor with reference electrode (above) and measuring electrode (below).



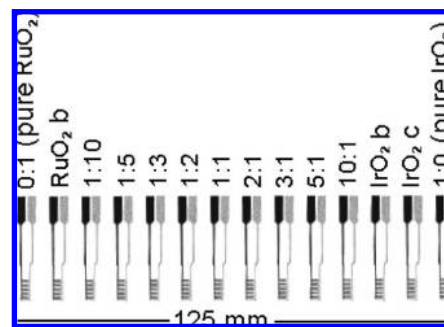
**Figure 4.** Measurement of single screen printed sensors with an additional conventional glass electrode to check the performance of the sensor: (a) ruthenium(IV) oxide; (b) iridium(IV) oxide.

resistive type gas sensors has been published.<sup>9</sup> This design though did not prove to be feasible in this special case: the high impedances of the pH sensors result in small currents in the range of a few nanoamps, requiring the apparatus to be well shielded to minimize parasitic effects on long conducting lines and external interferences. Therefore, a serial yet automated approach to the measurement was taken.

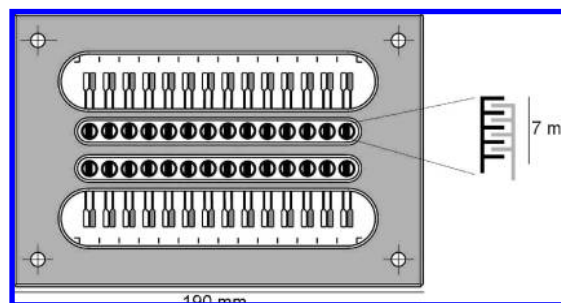
A substrate holder was constructed to accommodate the LTCC plate with the screen printed sensors (Figure 7).



**Figure 5.** Schematic drawing of the combinatorial screen printing process. Elastic barriers separate the individual pastes. A squeegee with gaps at the position of these barriers prints the sensors on the substrate.



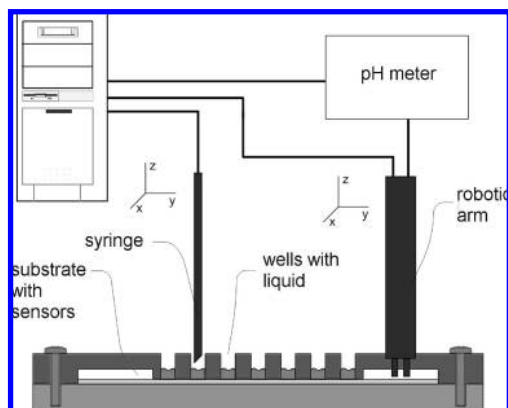
**Figure 6.** Substrate with varying printing pastes. The ratios of weight percent  $\text{RuO}_2:\text{IrO}_2$  pastes are given as well as other pastes ( $\text{RuO}_2$  b,  $\text{IrO}_2$  b,  $\text{IrO}_2$  c) with a different organic composition.



**Figure 7.** Substrate holder for measuring liquids with screen printed interdigital sensors on a LTCC substrate.

Wedged between two steel plates (the upper one is shown in gray), each interdigital sensor was supplied with an O-ring sealed well accessible from above. This allows the variation of the liquid from sensor to sensor without interference of





**Figure 8.** Scheme of a robotic measurement device. The arm connects the sensors in a serial fashion with the pH meter. A steel needle which is also movable in the  $x$ - $y$ - $z$  direction allows the manipulation of the liquids in contact with the sensors.

the media. The upper steel plate was also cut out to make access possible to the connecting pads of the individual sensors.

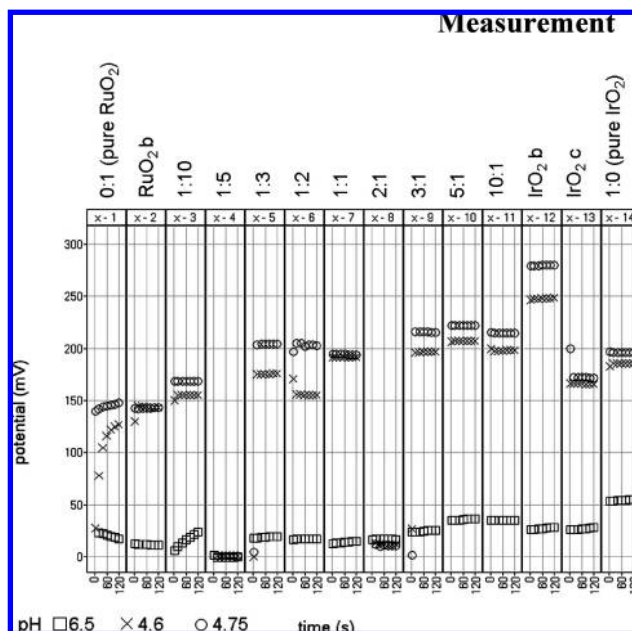
Figure 8 shows the schematic drawing of a robotic measurement arm with direct coaxial connection to a pH meter. Attached to the downside of the robotic arm are two pins which connect the pH meter via the coax line to the pads of the measurement and the reference electrode, respectively. The robotic arm also serves a second purpose. A laboratory syringe system is fixed to it, allowing to dispense liquids in the magnitude of microliters. Using this dispensing system, it is possible to manipulate the liquids in the wells above the sensors automatically, e.g. dispensing acid to lower the pH of the medium. The sensors are therefore treated sequentially: the arm moves to the first sensor, adds water to the well, measures the potential of the sensor, adds acid to the well, measures the potential of the sensors etc.; it then moves to the next sensor and repeats the process. The movements, the measuring and dispensing process are fully automated and controlled by a single PC unit.

### Measurement

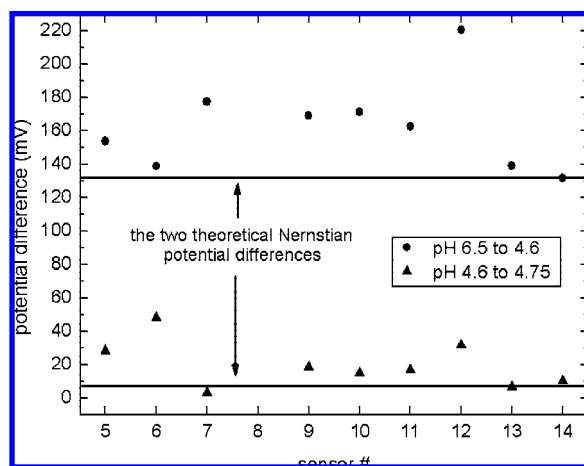
A measurement of the 14 sensors with composition of measurement electrodes as above is shown in Figure 9. The three signatures correspond to three measurements: pure water ( $\square$ ), pH = 4.60 ( $\times$ ), and pH = 4.45 ( $\circ$ ). The sensors 4 and 8 were short circuited and did not show any potential difference between measurement and reference electrode.

Sensor no. 1 (pure ruthenium(IV) oxide) exhibits a similar behavior like the single sensor shown in Figure 4. The potential is less stable and does not reach a steady value. Adding only a small amount of iridium(IV) oxide changes this behavior though. The pure water value still does not reach a state of equilibrium, but the two subsequent measurements with lower pH do. Also, a tendency is visible that with growing iridium(IV) oxide content the potential is shifted to higher values.

Of the sensors that show a stable potential, the potential differences between the measurements at pH 6.5 and 4.6 and the measurements at 4.6 and 4.75, respectively, are shown in Figure 10. The solid lines represent the theoretical Nernstian potential differences of 133.1 and 8.8 mV,



**Figure 9.** Measurement of the screen printed sensors shown in Figure 6. The sensors were consecutively measured. The compositions of the sensors are given above the diagram.



**Figure 10.** Potential differences between the values of pH 6.5 and 4.6 and pH 4.6 and 4.75, respectively, of the individual sensors that show a stable potential. The solid lines represent the theoretical Nernstian behavior.

respectively. Sensors with a composition other than pure iridium(IV) oxide (no. 12 and 13) exhibit a supra-Nernstian behavior.

This is attributed to a nonstoichiometric composition of the oxide.<sup>4</sup> The metal-to-oxygen ratio differs from the stoichiometry 1:2. In this case it seems to stem from the ruthenium(IV) oxide, as the result for pure iridium(IV) oxide is in close accordance to the theoretical Nernstian behavior.

The best result is shown by sensor no. 12 which is pure iridium(IV) oxide paste with organic composition of type b. Although the trend observed in the potential dependence on the pH may be understood in qualitative manner, the scattering of the data as well as the absolute potential values are expected to be determined by the microstructure of the respective material as well. The microstructure itself depends on the complex interplay of several process parameters, and even a constant pretreatment and fabrication process, as

performed in this work, does not necessarily lead to the same microstructure in the final material.

### Conclusion

A variation of printing pastes on one substrate using only one printing process to print sensors with different pastes has been realized. It therefore greatly reduces time for the preparation of such substrates. Also, as these sensors can be tested side by side, it eases the testing of different sensor materials. The robotic measurement device in combination with automatic manipulation of fluids to evaluate the performance of the sensors printed in the manner shown above makes a rapid testing possible. Ongoing works at Bosch Laboratory Systems evaluate the shown process and also the possibility of automatic preparation and mixing of screen printing pastes.

### References and Notes

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