Redox Sensors for the Control of Process and Waste Waters

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Abstract**—The state of waste and process water depending on the particular application can be characterised by quantitative analysis of its composition (e.g., heavy metal ions, nitrate or phosphate) but often, at least in a complementary manner, by determinating of non-specific parameters like electrolytic conductivity or redox potential. The latter is usually measured potentiometrically using indicator electrodes of precious metals. However, their application is connected with measurement errors caused by interactions between the media and the noble metal surfaces. Specifically this problem occurs in real media that can be found in process chemistry and in waste water sector, for example. Using electron conducting glass instead of noble metal membranes in potentiometric redox electrodes solves this problem. We present possibilities for their fabrication and results from their use.**

Keywords-redox potential; sensor; glass membrane; thick film; thin film; potentiometry

I. INTRODUCTION

The redox potential, also denoted as oxidation reduction potential (ORP), is a measure for the ability of an aqueous system to take up electrons from a chemical reaction or to give up electrons. The ORP of a system can be changed by the addition of substances unless they are oxidative or reductive. Determination of redox potential is very important in nature and technology as it characterises the present state of a system. Additionally, ORP can be used as controlled process variable for the performance of technical reactions.

As control variable it is essential, e.g., for the water treatment as in many cases it is comparable to the pH value. Temperature, ionic strength and pH value are all important contributing factors. Studies have shown that the lifetimes of bacteria and other microorganisms are also strongly dependent on the ORP of the media.

Currently, noble metal based electrodes (mostly in compact embodiment according to standards) [1, 2] are predominantly used for the determination of redox potentials, while occasionally, electrodes based on film technology or electroplating [2] are used. Independent of the shape of the noble metal indicator electrode, potentiometry is used for the redox potential determination. The material of the measuring electrode is critical for the results. Typically, gold, platinum or palladium are used in their construction.

Gold electrodes react to chlorides and cyanides present, while platinum electrodes do not. Instead, in reducing solutions together with palladium they form hydrides. This impacts the electrode properties, particularly the absolute position of the potentials measured in analyte solutions with the redox electrodes, as well as the adjustment behaviour of the potentials in case of composition changes in the measured media. In addition to the poor reproducibility of noble metals electrodes, successive measurements are subject to an additional measurement uncertainly of ± 25 mV.

The electrodes become unusable when catalytic poisons such as SO_2 or other sulfur compounds reach their surface. Proteins also cause an inactivation of noble metal surfaces and the presence of gaseous oxygen or hydrogen in the test medium influences the half cell potential. Precious metals can act as an undesired catalyst, e.g., they promote the decomposition of hydrogen peroxide. Precious metals are expensive meaning and a substitute is highly desirable. Investigations of cheaper carbon electrodes (e.g., graphite electrodes) have shown that a high reproducibility of the electrode potentials is very difficult to achieve; therefore, they are not an adequate alternative.

The problems of precious metal electrodes can be circumvented by using glasses with very high electron conductivity. Such glasses were first investigated at the end of the 1970s [3]. These electrodes operate based on the presence of iron and titanium oxides in the glass, whereby in the case of Ti the metal coexists in the oxidation states +3 and +4 in a predefined proportion. Currently, redox glass electrodes are based on platinum wires covered with redox glass [3] or prepared analogously to conventional pH glass electrodes [4]. However, it is rarely possible to handle the special glasses which readily crystallise by the glass blower. The thermal coefficients of expansion are incompatible, in general, with those of usual electrode shaft glasses, inevitably leading to high wastage rates. For some niche uses it is reported about results of their application [5]. Recently published works deal with the use of thick film [6] and thin film technology [7] as new manufacturing technologies for redox glass based indicator electrodes.

Previous solutions for the measurement of redox potentials in this and other process waters in circulation were based on the use of noble metal indicator electrodes, solely.

The above mentioned drawbacks were accepted. Alternatively, a bioactivity sensor (BAS) [8, 9] was developed, based on the principle of a biofuel cell. The electron transfer from the biological component to the anode of the sensor was used for analytical applications. An application in the practise is not given currently.

In this paper a new glass based system for the determination of the redox potential is introduced. The paper is organised as follows. The motivation for the development of new a redox sensor system and its use in paper industry processes is outlined in Section II. Section III describes manufacturing of the planar redox glass electrodes in thick film technology. First results of measurements with this multisensordevice as a part of a process water analyser are demonstrated in section IV. Additionally, we introduce a procedure to extend the lifetime of the measurement system. The conclusions and acknowledgement close this article.

II. PROBLEM

In the production of paper, water is required for auxiliary and cleaning purposes and it is often used several times. Beside the raw materials, the production details are critical to the quantity and composition of the sewage. In general, ecological and economic considerations lead the paper industry to reduce the sewage it produces. In reducing the volume of waste water the proportion of soluble substances increases, creating an undesirable nutrient-rich habitat for micro-organisms. This leads to an increase of slime and biofilm growth in the system. The problem is treated effectively by an optimised application of biocide active substances. In any case, an efficient sewage treatment with biological stage of degradation is necessary. Further reduction of sewage volume necessitates an enlargement of the biological sewage treatment arrangement with biofilters. For the controlled addition of peroxide based biocides to suppress the slime growth in the process water, redox potential determination can make an essential contribution, whereby the complicated composition of the medium does not require the use of precious metal electrodes.

For the assessment of the determined redox potentials it has to be taken in account that beside the concentration of the biocides the position-dependent amount of oxygen and/or the pH values have a significant influence on the sensor signal. These parameters should additionally be determined and considered for the evaluation of the redox potentials.

III. SOLUTION

First a glass mixture consisting of SiO_2, Na_2O, CaO, Li_2O, Fe_2O_3, and Fe_3O_4 was prepared according to [10], homogenised, melted in a high temperature chamber furnace at 1400 ^{o}C and processed into rods. These were milled in a planetary ball mill. Afterwards, the resulting powder was sieved through a mesh, weighed, blended with the identical amount of a terpineol containing binder and mixed again in the planetary ball mill. To fabricate planar thick-film sensors, a circular electrode structure of platinum with a thickness of 8 μm was screenprinted on an alumina substrate, dried and fired. For the redox-sensor fabrication by thick-film technology the sensitive pastes and covered substrates were heated to decrease the paste-viscosity and to simplify the application of the pastes onto the substrates. Then, the glass paste was carefully applied to the substrate. After drying at 150 ^{o}C in an oven with recirculating air the sintering process was executed. The resulting redox glass membrane had a thickness of 40 … 100 μm.

For the application of the electrodes in process water, the glass coated substrates were assembled in a high-grade steel case and equipped with a protective hood. As reference electrode for the measurements, a solid state electrode with an epoxy-membrane filled with KCl according to [11] was used. Figure 1 shows both electrodes separately assembled.

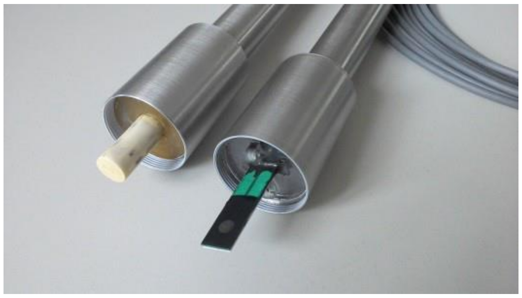

Figure 1. Glass based redox potential probe (right) and polymer based reference electrode (left) for the industrial application

They were placed in measuring lances, where additional electrochemical sensors (T, pH, pO_2) also were installed. Data collection is possible at different places within the water cycle and as can be seen in Figure 2, it can also be measured beyond this circulation system after sample collection by means of pumps.

Figure 2. Measuring system for the monitoring of process water, consisting of control box (a), Measuring lance (b) and measuring barrel (c)

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The cleaning of contaminated sensors occurs in the measuring tube under the following conditions:
The measuring tube represents a current-optimised flow measuring cell with minimised volume and ¾“ hose connection delivering a high-enough current. This minimises the slime and biofilm growth in the sensors and inner surfaces of the measuring cell. Without measuring tube, the measuring lance can be used as a multi-parameter insertion probe in large containers. The compressed air is provided by an autonomous small compressor. A compressed air nozzle was placed for every sensor to clean the sensitive surfaces. The number and the duration of the cleaning impulses can be adapted for every sensor of the respective load of the measuring solution. The cleaning cycles should be chosen so that biofilm formation is avoided. The inflow can be interrupted by an added electromagnetic valve to detect the biological load of the process water by the oxygen reduction per unit time and the change of the redox potential. The efficiency of the cleaning procedure is demonstrated in Figure 3.

Figure 3. Multi sensor system to control process water of the paper industry left contaminated; right after cleaning with compressed air

The results obtained by means of the continous use of multisensors during the paper manufacturing process at different places of the water cycle system enable the plant operators to judge the state of the system and its biological contamination (slime growth). The focus lies on the measurement of redox potentials by means of glass-based electrode.

IV. RESULTS

We present results of the multisensor-equipped measuring lances in model waters and in process water of the paper industry with particular focus on the innovative new redox glass electrodes. As a paper mill typical model medium, a solution of $CaCl_2 * 6\ H_2O$, $Na_2SO_4 * 10\ H_2O$, starch and NaCl was prepared. The influence different biocides have on the electrochemical measurements if no micro-organisms exist in the solution was examined. The biocide Wofasteril E 400 was used and Figure 4 shows it has a clear effect. For the investigations, different electrode types were used. In addition to the glass-based redox electrodes, conventionally made pH glass electrodes and a platinum sheet for referencing redox measurements were taken. The pH electrode exhibits a decrease of the pH value with the addition of the peracetic acid based biocides, as is expected. The redox glass electrode records the change of the redox potential as a result of the biocide addition. The fact that the potential change with the platinum sheet also acting as a redox electrode does not precipitate so high, can be traced back on its known pH dependence. Figure 5 shows the results of own investigations into the pH dependence of the measurements.

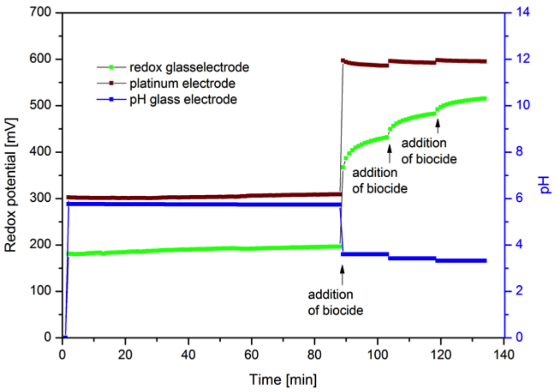

Figure 4. Changes of potential and pH value when biocide is added to a paper mill typical model solution

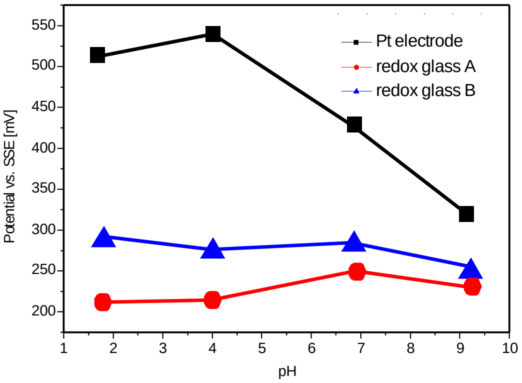

Figure 5. pH dependence of ORP for different redox electrodes

Figure 6 displayes an exemplary measurement of process water in a paper factory. Besides the redox potential which was measured using both a platinum and a glass electrode, the oxygen content as well as the temperature are shown. The sensors were installed in the measuring lances shown in Figure 3. The electrodes were automatically cleaned by means of compressed air every 12 hours, corresponding to 4, 16, 28, 40 and 52 hours in Figure 6.

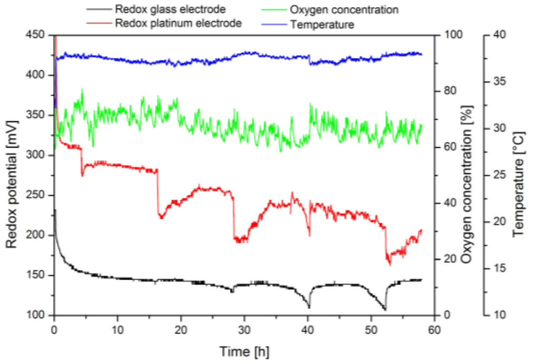

Figure 6. Course of redox potential, oxygen content and temperature in the process water of a paper mill (automatic cleaning cycle: 12 h)

The oxygen concentration as well as the temperature are nearly constant in Figure 6. The redox potential curves partially deviate by more than ~100 mV from each other due to the cross sensitivity of the platinum electrode to components in the process water. By means of the redox potential, determined with the redox glass electrode, contamination caused by the microbial load of the process water can be determined. At the beginning of the measurement the redox potential appears to a roughly steady level of about 150 mV. Over longer timespans, the influence of the automatic cleaning by means of compressed air becomes more pronounced. The cause is the biofilm that forms on the electrodes as a result of the microbial contamination, which lowers the redox potential. The cleaning removes this and the original potential can be reached again. The platinum electrode is influenced immediately by the cleaning with compressed air, because this reacts to the aerial oxygen. This precious metal-based electrode is therefore completely unsuitable for measurements in process waters of paper mills.

CONCLUSION

Target of the development was the realisation of redox glass electrodes to overcome some problems of noble metal electrodes like inhibition and catalytic side reactions. Results of the application of thick film redox glasses based on Ti- and Fe-oxides are presented in this paper. They are suitable for the requirement of process water in paper industry. As a part of multisensor devices the planar electrodes have successfully been used for the controlling of biocide input in industrial paper processing. This sensor system enables the save prevention of unwanted slime and biofilm growth in paper production processes without biocide overdosage.

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