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Glass based redox sensor

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Abstract:

Introduced is a glass based planar sensor for the determination of redox potentials. The sensor was fabricated by applying and stoving an iron-containing paste on an alumina substrate partially covered with a platinum layer. Regarding the condition of the functional glass layer, it was characterized using several physical and chemical methods. Furthermore, the determination of redox potentials was carried out with different redox active substances. The results obtained with these electrodes were comparable to those received with conventional noble metal based redox electrodes. A significant pH dependence of the measurement signal was not detected. Moreover, the electrode could be used as working electrode for cyclic voltammetry, too.

Key words: Redox potential, glass electrode, thick film technology, potentiometry

Introduction

Presented is a glass based planar sensor for the determination of redox potentials. The sensor was fabricated by applying and stoving an iron-containing paste on an alumina substrate partially covered with a platinum layer as conductive path. Regarding the properties of the functional glass layer, it was characterized using several physical and chemical methods. Furthermore, the determination of redox potentials was carried out with different redox active substances. The results obtained with these electrodes were comparable to those received with conventional noble metal based redox sensors. A significant pH dependence of the measurement signal was not detected. Moreover, the electrode could be used as working electrode for cyclic voltammetry, too.

Experimental

Glass-making

To produce the redox glasses a batch of SiO2, Na_2O, CaO, Li_2O, Fe_2O_3 and Fe_3O_4 of different mixing ratios was prepared, homogenized, molten in a muffle furnace using a covered platinum crucible at 1400 °C and poured in a graphite channeling.

Paste preparation

The finished glass was mechanically processed and milled in a planetary ball mill for one hour. Afterwards, the pretreated glass powder was sieved through a gage, weighted, blended with the identical amount of a terpineol containing binder and mixed again in the planetary ball mill for further 16 hours.

Sensor fabrication

For the sensor fabrication by thick film technology the prepared paste was transferred in a glass jar. Then, paste and alumina substrates were heated to 50°C to decrease the viscosity of the glass paste and to make their application on the substrate (0.6 cm x 5 cm, thickness: 0.63 mm) easier. Beforehand, a thick film structure of Pt with a thickness of 6 - 8 µm was realized on the substrate. The paste was carefully applied on the substrate in such a manner that the circular platinum area (∅ 0.5 cm) was covered completely. After drying at 150 °C in an oven with recirculating air the sintering process therefore was executed in a heating oven. As a result a functional redox glass membrane with a thickness of 40 … 100 µm was obtained.

BET Surface analysis

Normally, the specific surface of solids is determined by adsorption isotherms. They show how much gas is condensed or adsorbed on the surface of a sample under standardized pressure and temperature conditions. These investigations are often carried out with nitrogen. For the analysis only one measurement up to a relative pressure $p/p_0$of 0.3 is necessary because in that area the formation of the mono layer is finished. From the amount of gas that is needed to cover the surface and from the space requirement of a single gas molecule the specific surface of a sample can be calculated. The measurements were carried out with the device SA 3100 of COULTER.

Particle size determination

The particle size determination is based on the principle of laser diffraction. Here, the property of all particles to diffract an incoming ray of light depending on their dimension is used. An increasing particle sizes amongst others result in a diminishment of the diffraction angles. For the analyses the device LS 230 of COULTER with a measuring range from 0.04 … 2000 µm was used.

Thermal analysis

The determination of the linear thermal coefficient of expansion (α) was carried out using the device DIL 402/4/G of NETZSCH. As sample mounting system we used quartz proven to be effective in a temperature range from 20 … 1000°C. The samples had a length of 24 … 26 mm and under the atmosphere air the heating rate was 5 K/min. The glass rod to be investigated was clamped between an end point and the quartz rod. The temperature sensor was brought close to the sample. The length change was detected inductively.

The thermogravimetric investigations were carried out with the device Setsys TG-DTA 12 from SETARAM. Two platinum crucibles and a quartz insert were used to investigate the molten glass samples short-term. One of the crucibles was filled with a known mass of the sample. The other crucible served as reference and was empty. Both crucibles were placed on a tray with temperature sensor to measure the heat flow during the experiment. The atmosphere consisted of synthetic air; the current velocity was approximately 1.6 L/h. The measurement was started at a temperature of 30 °C and elevated to a final temperature of1200 °C. The heating rates were 10 K/min (30 … 1000 °C), 5 K/min (1000 – 1100 °C) and 3 K/min (1100 – 1200 °C). Than the sample was cooled. All obtained values were corrected by means of base line data (blind measurement). The weight of the test sample was 23.3 mg.

X-ray investigations

X-ray investigations were carried out with the thick film electrodes by means of XRD. Therefore, for several measurements a powder diffractometer XRD 7 from SEIFERT (GE Inspection) with a CuKα radiation of a wave length of 1.5418 Å was used. The X-ray tube was operated with 40 kV and 40 mA. The measurements were performed with a counting period between 8 and 30 seconds per test point and a step size of 0.03°. Other samples were investigated with the device XRD 3003TT (also from SEIFERT) with a CoKα radiation of a wave length of 1.78901 Å and operation conditions of 40 kV and 30 mV for the X-ray tube. In these cases the counting period per test point was 30 seconds and the step size also amounted to 0.03°. The quantitative results were calculatedfrom the diffraction measurement by means of structural data and device parameters.

Measurement of catalytic activity

The measurement of the catalytic activity was carried out in a controllable, temperature programmable tube furnace of HTM REETZ. Within the oven a quartz vessel with a diameter of 15 mm was located to hold the sample. The oven was pruged with synthetic air with a hydrogen content of 1000 ppm. Diluted gases were used to avoid a strong heating of the sample. The temperature was decreased stepwise whereby in each case a constancy of the temperature was awaited. On the furnace outlet a FTIR spectrometer NICOLET 8700 of THERMO SCIENTIFIC was placed to determine the mass of the reaction product water for the evaluation of the catalytic activity.

Impedance measurements

To compare the internal resistances of the different redox glass electrodes impedance measurements were performed. Therefore, an Ag/AgCl reference electrode, a platinum counter electrode and the redox glass electrode as working electrode were inserted in a mixture of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ (ratio of ingredients: 2:1) in a measuring chamber acting as Faraday cage. The voltage amplitude was 20 mV and the measuring range 10 kHz – 100 mHz. The impedance measurements were carried out with a VersaSTAT 3 and the evaluation of the results with the software VersaStudio of PRINCETON APPLIED Research.

Cyclic voltammetry (CV)

For the determination a potentiostat-VersaSTAT 3 was used again. At first, 25 mL of a 0.1 M KCl starting solution were used and further 5 mL KCl were added. The CV was carried out in a potential range between 0 and 1 V to determine the base current. Following, to a new 0.1 M KCl solution 5 mL 0.1 M $K_4[Fe(CN)_6]$ were added twice and a measurement was performed in each case. The same measuring procedure was executed for 0.1 M $K_3[Fe(CN)_6]$ solution. Finally, determinations in 2.5 mL of a 0.1 M$K_3[Fe(CN)_6]$ and of a 0.1 M $K_4[Fe(CN)_6]$ solution were performed. Comparable measurements with ferrocene were carried out. Therefore, a 0.01 M ferrocene solution and a

0.1 M tetra(n-butyl) ammoniumhexafluorophosphate solution in acetonitrile were prepared. Both solutions were transferred into a beaker glass as a 1:1 mixture and a cyclic polarization was performed between 0 and 1.5 V. The reference electrode was combined with an electrolyte bridge.

Determination of the redox potential

For the redox potential measurement and its evaluation the device LM Remote of SENSORTECHNIK MEINSBERG and the associated software were used. At first, mixtures of $K_3[Fe(CN)_6]$ and K4[Fe(CN)6] in ratios 2:1 and 1:2 were prepared. Afterwards, determinations have been proceeded in the 2:1, 1:2 and again 2:1solutions over periods of 30 min in each case.

Determination of the influence of the pH-value on the redox potential

The experiments were performed in two different buffer solutions (NBS) (pH_1= 6.86 and pH_2 =4.01 at 25 °C) over 30 min.

Results and discussion

Table 1 shows results of investigations from BET-, particle size- and dilatometric measurements of two redox glasses (glass A: SiO_2, Fe_2O_3, Li_2O, Na_2O; glass B: SiO_2, Fe_2O_3, Li_2O, C) also used for all following experiments. Further information concerning their detailed composition is given elsewhere [3].

Glass	BET-surface / m^2g^{-1}	Particlesize /µm	$\alpha/10^{-6}K^{-1}$ (at 200-300°C)
A	1.522	0.123	8.73
B	1.032	0.163	7.42

The mass loss of the glasses was low. Even at 1200 °C still 99.5 % of the initial mass remained. A small mass loss was observed in the temperature range between 350 … 500 °C. It can therefore be concluded that during the heating process no appreciable change of the glass and no out-gassing of components occurred. By means of DTA investigations several crystallization peaks were identified, indicating that beside an amorphous phase redox glasses also possess crystal structures. In particular XRD measurements showed (as expected) that the degree of recrystallization increased in the order initial glass - glass powder - thick film glass electrode membrane, whereby also for the last mentioned material the amorphous characteristics still dominated.

Measurements of the catalytic activity of redox glasses A and B showed that in this regard the drawback of conventional platinum based redox electrodes did not exist here. The water that was detected in the gas flow which escaped from of the device was a desorbate of the glass powder. The values of the electrode resistances of the thick film electrodes ranged from 1 to 100 kΩ. Fig. 1 and 2 demonstrate by means of CVs the functionality of the new sensors. The curves were obtained in ferrocene solution with different scan rates.

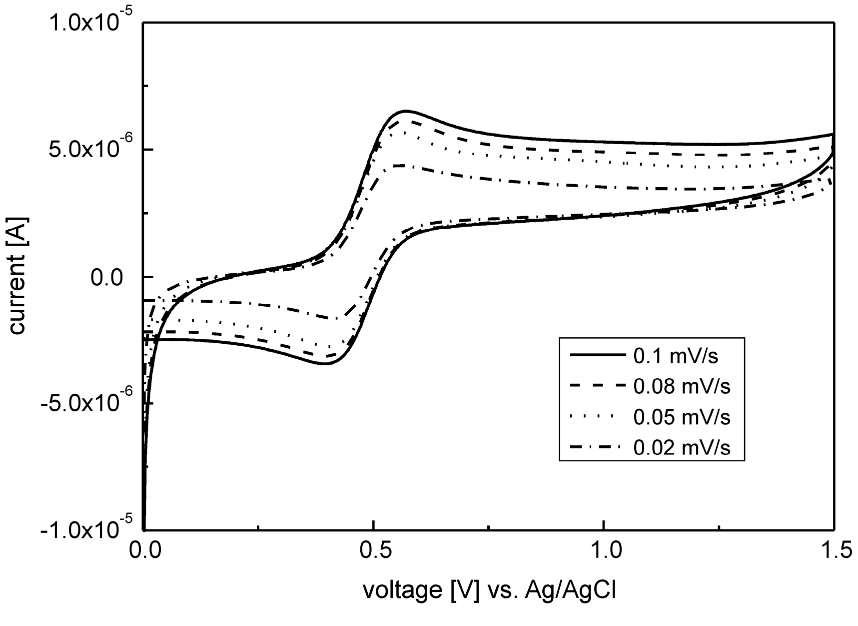

Fig.1: Cyclic voltammogram of a 0.01 M ferrocene solution in acetonitrile, conducting salt: TBAHFP scanrate: 0.1 V/s, 0.08 V/s, 0.05 V/s, 0.02 V/s, working electrode: glass A

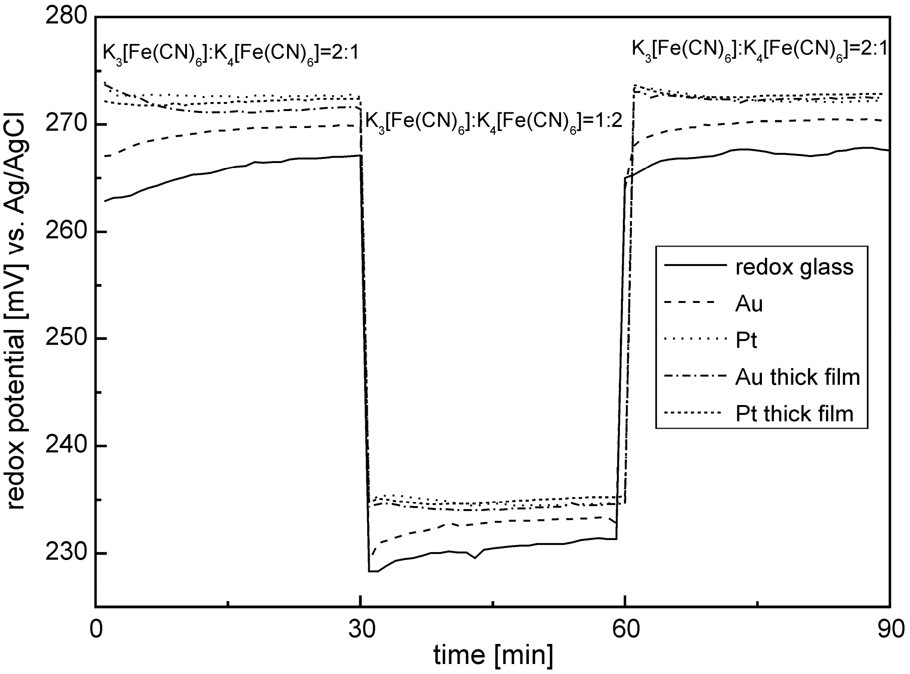

Fig. 2: Redox potential measurement with different conventional electrodes compared to a redox glass electrode (glass A)

Surprisingly, the redox glass electrodes had partially a clearly lower pH cross sensitivity compared to platinum based sensors. At the noble metal often a pH dependency can be observed, caused by the formation of platinum oxide layers on the electrode surface.

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References

[1] DIN 38 404 (Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung)

[2] B.P. Nikolskij, M.M.Schulz: US 3 773 642 (1971)

[3] W. Vonau, K. Ahlborn, F. Gerlach, B. Hahnebach, E. Pöhler: Elektrochemische Elektrode und Verfahren zu ihrer Herstellung. German patent 10 2011 118 409.4 (2011)