New Developments in Electrode Materials for Electrochemical Sensors

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Abstract. Electrode materials are the key components for electrochemical sensors which can be used for determination of gaseous and dissolved species. The sensitivity as well as the selectivity are mainly influenced by the kind and the structure of sensitive electrode material. In this paper two kinds of materials are described. Screen-printed carbon electrodes (SPCE) can be modified by thin layers of conducting polymers like Poly(3,4-ethylendioxythiophene) (PEDOT) and gold nanoparticles. By means of differential pulse (DPV) and square wave voltammetry (SWV) it is possible to determine biogene amine like dopamine in liquids of human bodies and explosives in ground water in the nM und ppb level, respectively. Polyaniline (PANI) can be used not only in normal temperature sensors but also in high temperature sensors. For the first time we could show that zirconia based sensors with PANI electrodes in which Nb_2O_5 or $FeCl_3$ and $Co(NO_3)_2$ are embedded are suitable to measure hydrogen and hydrocarbons in oxygen containing gases at 450 °C. The sensitivities of such electrodes are much higher than those of the usual applied oxide systems like Nb_2O_5 or $La_{0.75}Ca_{0.25}Mn_{0.5}Ni_{0.5}O_{3-\delta}$. Due to the availability and compactness of electronic devices electrochemical sensors with modified electrodes can be applied in stationary (potentiometric) and non-stationary (SWV or DPV) mode in field application.

Keywords: screen-printed carbon electrodes, conducting polymers, gold nano-particles, mixed potential sensor based on zirconia solid electrolyte, hydrogen, hydrocarbons, dopamine, explosives, square wave volammetry, differential pulse volammetry.

1 Introduction

Electrochemical solid electrolyte sensors based on yttria stabilized zirconia are suited for the in situ measurement of hydrocarbons, hydrogen and NO in oxygen

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containing gases e.g. in exhaust [1, 2] of automotive and industrial combustion processes. Mixed potential gas sensors in which a sensitive electrode for combustibles or NO and a non-sensitive electrode are combined can be used in the same gas atmosphere [3]. The simple construction as compared with amperometric sensors, however, requires electrodes with high sensitivity and selectivity.

During the past 10 years, many metal oxides have been tested on their sensing qualities in sensing cells. Miura et al. described experiments with spinel and perovskite type oxides AB_2O_4 (A = Zn, Ni, Cd and B = Mn, Fe, Cr) [4, 5] and ABO_3 (A = Ln, Ni, Y; B = Cr, Mn, Fe, Co, Ni) [5, 6]. We investigated the $La_{0.6}Ca_{0.4}Mn_{1-x}Me_xO_{3-\delta}$ (Me = Ni, Co, Fe) and have been found that the electrode material $La_{0.6}Ca_{0.4}Mn_{0.8}Ni_{0.2}O_{3-\delta}$ has the highest potentiometric response to NO at 500 °C [7].

Modified carbon electrodes were reported to measure bioactive compounds in liquids of human body [8]. There are a lot of efforts to improve the sensitivity by modifying conducting polymers in which gold nano-particles are embedded. But such electrodes are mainly hand made. Therefore their performances are statistically highly spread. Screen-printed (thick-film) technology has made it possible to establish a mass-production of inexpensive electrodes with controlled thickness, diameter and uniform quality.

Up to now, there is no information about conducting polymers as electrode material for high temperature sensors. It seemed to be impossible to use such materials at temperatures > 250 °C. In this paper we will show for the first time that polymers like PANI can be used up to 450 °C. Additionally, as a new oxide system for YSZ based sensors we investigate the system the series $Ca_{1-x}La_xTiO_3$ (x = 0.001 - 0.2).

In the second part we present results obtained with modified conducting polymers as an electrode for determination of dopamine and explosives like trinitrotoluene (TNT) prepared in industrial like screen printing technology.

2 Experimental

The conducting polymers were prepared as follows: Polyaniline (PANI) was chemically synthesized from aniline by oxidative polymerization using ammonium peroxydisulphate in an acidic media. 0.05 M of aqueous solution of aniline (different concentrations) in 1 M H_2SO_4/HCl (different concentrations) acid were mixed together in a 200 ml beaker containing 150 ml solution 0.1 M of aqueous solution of ammonium peroxy disulfate is added drop-wise into a stirring solution and then a solution of $FeCl_3$ and $Co(NO_3)_2$ in the ratio 0.75 : 0.25 was added during stirring condition. The stirring of the reaction mixture was continued 5 - 6 hours to ensure the completion of the reaction. Finally, the precipitate was filtered and washed repeatedly with distilled water until the filtrate was colourless and then it was dried under vacuum condition.

PEDOT, Poly(3,4-ethylendioxythiophene), was prepared electrochemically using an aqueous solution of monomers.

Following materials were prepared by using the oxide route: $Ca_{1-x}La_xTiO_3$ with x = 0.0015 - 0.2 by tempering the ground oxides at 1200 °C for 17 h. The sintered

materials were ground in ethanol over 8 h, characterized as powders and mixed with an organic binder for manufacturing of pastes for screen printing. After printing of electrode materials on slices of yttria stabilized zirconia (YSZ) of 0.5 mm thickness and 12 mm diameter the pastes were fired at 1000 °C for 1 h.

All powder materials were characterized with respect to their specific surface (BET, COULTER SA 3100), grain size (Laser particle sizer, COULTER SA 230), crystal structure (XRD, D8Advance, Bruker AXS) and catalytic activity (setup, described in [9]). Addionally thermo gravimetric investigation (TG, DTA Seteram) of pure and mixed polymers were performed.

The powders were mixed with an organic binder to get a printable paste. The printed layers were used without an additional firing process for high temperature sensors as well as for normal temperature sensors.

The screen-printed electrodes were tested with respect to their potentiometric sensitivity in different gas mixtures, containing O_2 and H_2 or hydrocarbons (C_3H_6, C_2H_4) respectively by using the experimental setups, described in Figure 1. The setup and procedure for mixed potential and conductivity measurements are given elsewhere [6, 9]. The YSZ disk with the freshly prepared polymer electrode was heated up to the operating temperature.

The normal temperature sensors shown in Figure 2 were applied in aqueous solution with increasing amount of TNT and dopamine, respectively.

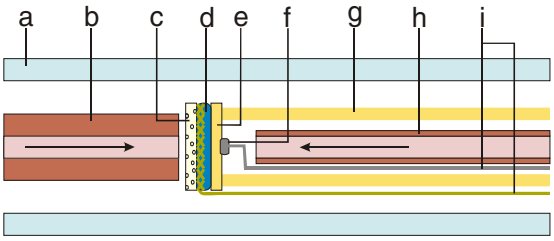

Fig. 1. Setup of YSZ cell with conducting polymer electrodes for potentiometric measurements a: Quartz tube, b: measuring gas, c: porose alumina disk, d: polymer electrode with gold net, e: YSZ-disk, f: Pt/air reference electrode, g: YSZ-tube, h: air supply, i: connecting leads

Fig. 2. Modifiable screen-printed carbon electrode for determination of dopamine and explosives in aqueous solutions

For the determination of the organic substances the well known electrochemical methods square wave voltammetry and differential pulse voltammetry were used. The case of dopamine determination 0.5 M ascorbic acid and 0.5 M uric acid were added in order to check the cross sensitiviy against other substances which are usually present in liquids of human body.

3 Results

3.1 A Structure and Morphology

An example of the morphology of modified screen-printed carbon electrodes is given in Figure 3. The picture shows that the surface of the polymer film is covered with gold nano-particles.

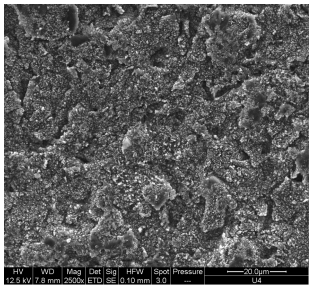

Fig. 3. SEM image of the screen-printed carbon electrode modified with PEDOT and gold nano-particles (Au-PEDOT-SPCE)

3.2 B Potentiometric Investigation

The potentiometric investigations in hydrogen and propen containing gases show pronounced sensitivtity of the conducting polymer containing electrode to low concentrations of gases as illustrated in Figure 4 and Figure 5. At higher concentrations a second process leads to a smalles increase of the signal.

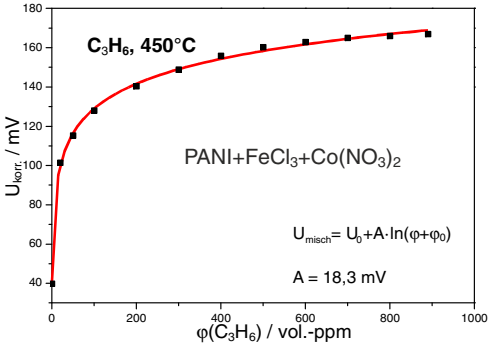

Fig. 4. Dependency of the potential on the C_3H_6-concentration of the YSZ cell with PANI electrode at 450 °C vs. Pt/air reference, oxygen concentration 1.5 vol-%

The voltage response after a jump in concentration is very fast (few seconds). Amazingly, the data obtained are very stable and reproducible over several days. For low concentrations of combustibles the sensitivity was found to be 3 mV/ppm C_3H_6. This is much higher than those obtained for mixed oxides electrodes. We found by means of TG/DTA investigations that a higher part of conducting polymer is decomposed and evaporated due to the thermal treatment at 450 °C. But the mass of the polymer is stable at this temperature for several days. Although the composition of the remaining part is not clear at the moment it seems to be that a net of organic structures was formed in which the inorganic species are embedded. Similar results were obtained for hydrogen as shown in Figure 6. The sensitivity for hydrogen was found to be 1.6 mV/ppm. The advantage of such polymer electrodes consists in the simple preparation without high temperature processes (up to 1200 °C) which are necessary in the case of oxide or mixed oxide electrodes.

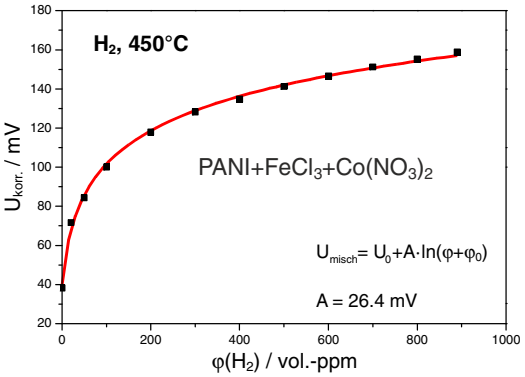

Fig. 5. Hydrogen concentration dependence of the mixed potential cell with electrode materials PANI- elctrode ϑ = 450 °C, flow rate 50 ml/min, vs. Pt/air reference, oxygen concentration 1.5 vol-%

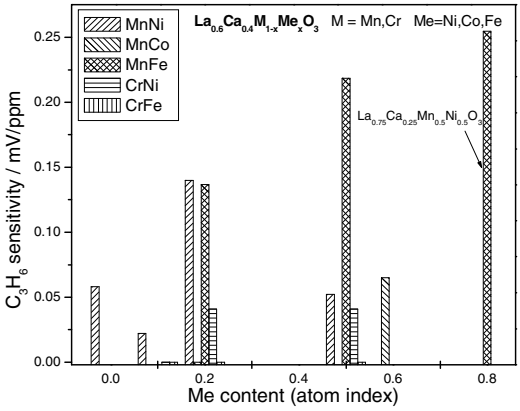

Fig. 6. Propen sensitivity for different perovskite electrodes at 550 °C, flow rate 50 ml/min, vs. Pt/air reference, oxygen concentration 1.5 vol-%

For comparison the results of the potentiometric measurements on $La_{0.6}Ca_{0.4}M_{1-x}Me_xO_{3-\delta}$ (M = Mn, Cr; Me = Ni, Co, Fe) electrodes, using C_3H_6-O_2-N_2 containing atmosphere are given in Figure 6. The Ni and Fe containing manganites in all compositions show a much lower sensitivity to C_3H_6 (up to 0.25 mV/ppm). The sensitivity values of the Fe manganites are higher than those of the Ni manganites [7].

In the investigated system $Ca_{1-x}La_xTiO_3$ a series of compound with high concuctivity could be prepared. Figure 7 shows the temperature dependence of the conductivity in Arrhenius like plots. Used as an electrode material they behave as equilibrium electrodes. That means combustibles react with oxygen in non equilibrated gases. Therefore those compounds are non siutable for mixed potential sensors.

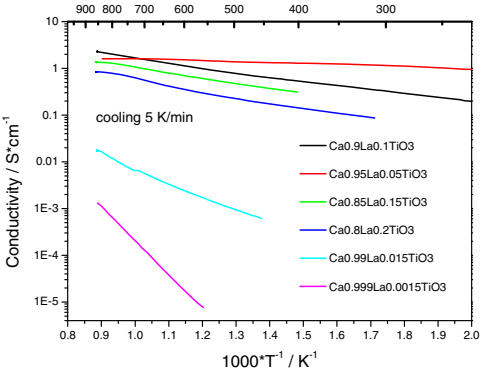

Fig. 7. Arrhenius plots of conductivity in the system $Ca_{1-x}La_xTiO_3$

3.3 C Voltammetric Results

Modified conducting polymers can be successfully applied to improve the sensitivity of carbon electrodes for dissolved bioactive species like dopamine and to reduce the cross sensitivity against other substances found in liquids of human body like ascorbic and uric acid. These modifications can be performed in one step easily from aqueous solutions under definite electrochemical conditions with high reproducibility.

The Figure 8 shows the square wave voltammograms of solutions containing 0.5 mM AA + 0.5 mM UA and various concentrations of DA in 0.1 M PBS (pH 7.4) at Au-PEDOT-SPCE. The Figure 9 shows the calibration curve between the peak current and concentration of dopamine. Due to the modifying of PEDOT modified screen-printed carbon electrodes (PEDOT-SPCE) by means of gold nano-particles, the sensitivity for dopamine was increased significantly to 19.9 $\mu A \mu M^{-1}$ on Au-PEDOT-SPCE in comparison to 0.311 $\mu A \mu M^{-1}$ on PEDOT-SPCE.

In the clinical relevant range from 10 nM to 2 µM dopamine the sensitivity was found to be 19.9 µA/µM. The sensitivity of the modified SPCEs for the determination of dopamine did not change after storage in air or in 0.1 M PBS (pH 7.4) for at least 2 months. This offers the possibility to produce such sensors in a large scale and makes attractive for their application in doctor's practice.

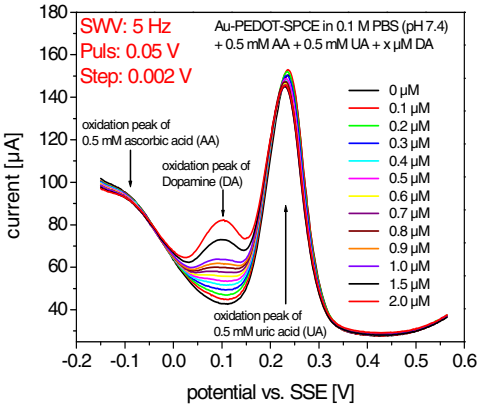

Fig. 8. Determination of dopamine (for concentrations 0.1 - 1.0 in steps of 0.1 and 1.5 and 2 µM, left peaks) in the presence of 0.5 mM ascorbic acid + 0.5 mM uric acid (right peak) at gold and PEDOT modified screen-printed carbon electrodes (Au-PEDOT-SPCE) by SWV

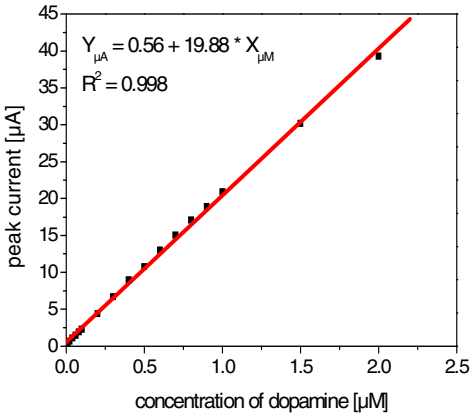

Fig. 9. Plot of the peak current vs. concentration of dopamine (calibration curve)

The determination of explosives like trinitrotoluene (TNT) in soil of abandoned military training areas is an important task. We could show in Figure 10 that such compounds are electrochemical active species which can be reduced elcectrochemically in two steps on unmodified screen-printed carbon electrodes.

Nowadays, well known quasi-stationary electrochemical methods like differential pulse and square wave voltammetry can be performed using small and inexpensive devices in field application. That makes the use of printed electrodes very attractive.

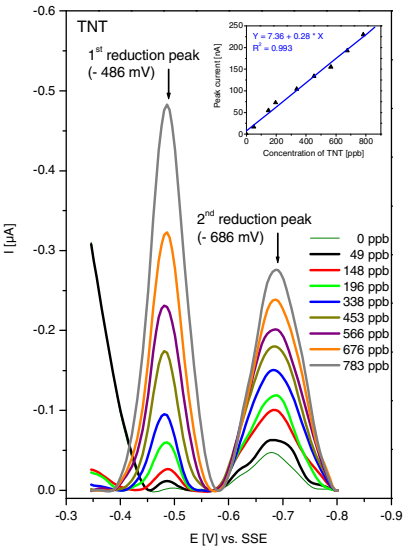

Fig. 10. Determination of TNT on screen-printed carbon electrode (SPCE) by DPV in 0.1M KNO_3/0.1M KCl solution (counter electrode Pt)

4 Conclusions

For the first time new electrode materials from the group of conducting polymers were successfully tested in solid electrolyte sensors based on YSZ. Surprisingly, it was possible to measure reproducibly mixed potential in dependence on concentration of combustibles at 450 °C over several days. We found as compared to electrodes made of mixed oxides a markedly enhanced sensitivity to C_3H_6 and H_2. For Fe^{3+} and Co^{2+} modified PANI the maximum sensitivity was found of about 3mV/ppm C_3H_6 at 450 °C. Further investigations of electrode materials and their structure and composition should give more information necessary for the development of taylored electrode materials. Carbon electrodes modified by PEDOT and PEDOT/Au can be succesfully applied using differential voltammetric methods to measure dopamine in presence of ascorbic and uric acid up to 0.1 µM with a sensitivity of 19.9 $\mu A \mu M^{-1}$. Such electrodes can also used for determination of dissolved explosives like TNT in ppb-level.

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