

Polymer based materials for solid electrolyte sensors

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ABSTRACT

Electrochemical solid electrolyte sensors based on Yttria Stabilised Zirconia (YSZ) with mixed potential electrodes are suited for in-situ measurements of low concentrations of combustibles like hydrogen, carbon monoxide or hydrocarbons and also nitrogen oxides. The parameters sensitivity, selectivity and long-term stability of these sensors are correlated mainly with the performance of the electrode material. This work is directed on the investigation of newly developed conductive polymer composite materials (CPC) based on polyaniline (PANI). These materials have been characterised with respect to their morphology, thermal stability, catalytic activity and electrochemical behaviour on solid electrolytes in gases containing hydrogen, ethene and propene. For the first time it could be demonstrated, that CPC, consisting of PANI and different metal oxides or metal salts can be used at high temperature measurement up to temperatures of 450 °C because of improved thermal properties.

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1. Introduction

Electrochemical solid electrolyte sensors are suited for the reliable, highly sensitive and rapid measurement of different gases in hot environments and also applications at lower temperatures [1]. Important sensor parameters like sensitivity, selectivity and long-term stability are correlated mainly with the performance of the electrode material [2]. During the last two decades extensive efforts were directed especially on the development of new electrode materials for mixed potential sensors [3–5], which are based on the kinetically controlled electrochemical conversion of oxidizable gases with oxide ions from the solid electrolyte [3,4]. Despite this intensive work there is still a considerable variety of potential applications for these sensors, which cannot be addressed due to insufficient sensor performance. One of the most important issues concerns the long-term stability [6,7], which is still critical for measuring electrodes based on gold and other noble metals if measuring times of several months without calibration are strived for. Therefore, new conductive fillers for composite mixed potential electrodes are needed, which provide sufficient electrochemical activity, thermal stability and low catalytic activity. This work is focused on the preparation of new composite materials for mixed potential

sensors made of conductive polyaniline (PANI) filled with different metal oxides or salts such as Nb₂O₅ or FeCl₃ and Co(NO₃)₂ during the polymerisation process. Intrinsically conducting polymers such as PANI have been the subject of extensive theoretical and experimental studies in recent years [8]. By filling the polymer with i.e. metal oxides, the thermal stability of the resulting conductive polymer composite (CPC) could be improved significantly. Because of its relatively high thermal stability, low costs, ease of synthesis and good environmental behaviour, among the conductive polymers PANI is most suited for this purpose [9–15].

The synthesised new materials have been characterised with respect to their thermal stability, their structure and morphology, their catalytic activity and their sensing behaviour in different non equilibrated gas mixtures in correlation to their impedances.

2. Experimental

Pure PANI has been prepared by two different methods. One method is described elsewhere [16], the other one serves as point of departure for synthesising the polymer composites. It includes the introduction of 0.1 mol aniline into 1 M HCl and the following polymerisation by adding 0.05 mol ammonium peroxodisulfate solution. The polymerisation of aniline in an acidic medium results in the formation of a protonated, partially oxidised form of PANI, the conductive emeraldine salt 4 (Fig. 1).

Two composites have been prepared by adding Nb₂O₅-powder to the solution described above before and after starting the polymerisation respectively. The molar ratio aniline/Nb₂O₅ has been adjusted at

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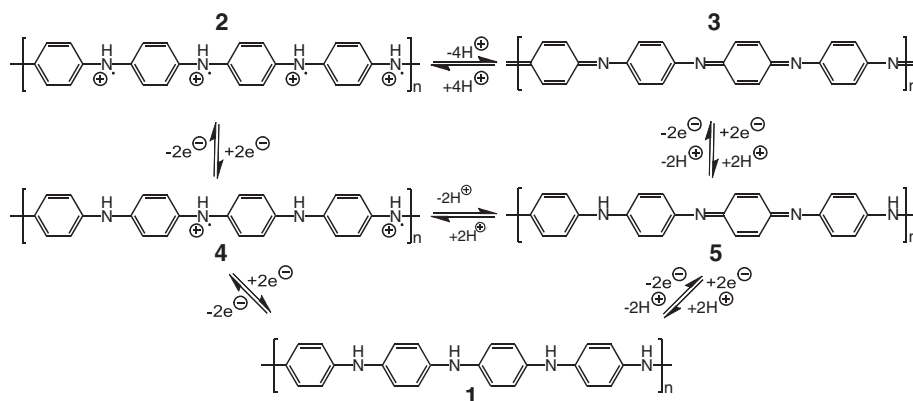


Fig. 1. Different forms of polyaniline. 1 leucoemeraldine (PANI, white/clear), 2 pernigraniline (salt) (PANI-PS, blue), 3 pernigraniline base (PANI-PB, violet), 4 emeraldine salt (PANI-ES, green), 5 emeraldine base (PANI-EB, blue).

2:1. After stirring for 14 h, the precipitates have been washed till the pH-value of the wash water reached pH = 4. To characterise the effect of washing procedure a further composite has been prepared additionally, where the Nb₂O₅ was added after starting the polymerisation, but washing the precipitate less intensively than the two other CPC till a colour change from green/white to blue/white. A last composite has been prepared by adding 0.075 mol FeCl₃ and 0.025 mol Co(NO₃)₂ to the solution after starting the polymerisation of aniline. This composite was washed till the wash water became colourless.

All materials have been characterised with respect to their specific surface (BET, COULTER SA 3100), grain size (Laser particle seizer, COULTER LS230), structure (SEM, Quanta 200, FEI and TEM, Philips EM 208), thermal stability (Setsys TG-DTA 12, Setaram), conductivity and catalytic activity. The catalytic activity was investigated by measuring propene oxidation at powder samples with the absolute surface of 2 m² in a gas mixture, containing 0.5 vol.% C₃H₆ and 2.5 vol.% O₂ by quantifying CO₂ formation at increasing temperature levels with an FTIR-spectrometer (NICOLET 8700, Thermo Scientific). The experimental procedure of the catalytic investigations is described elsewhere [17].

Pastes have been made by mixing the powders with a commercial binder (ESL Europe, 242SB) based on an epoxy resin and printed on YSZ tubes. Alternatively, a binder based on cellulose acetate was tested. These types of binders are commonly utilised in thick film technique. The binders strongly influence printing results and therefore layer morphology. They have to be removed during drying or firing procedures at elevated temperatures. The electrodes were dried 1 h after printing at 150 °C and investigated with potentiometric measurements against a platinum air reference at the inner side of the YSZ tube according to the experimental setup, shown in Fig. 2. The potentiometric measurements were carried out at 450 and 500 °C in different gas mixtures, containing 1.5 vol.% O₂ and 0 ... 890 vol.ppm H₂ or 0 ... 890 vol.ppm C₃H₆ in N₂, applied at the flow rate 50 ml/min at standard conditions. Moreover, a gas mixture, containing 3.9 vol.% O₂, 7.2 vol.% CO₂ and 0 ... 19 vol.ppm C₂H₄ in N₂ was used for the potentiometric investigations.

3. Results

3.1. Structure and morphology

The preparations of pure PANI as well as those of the composites result in agglomerates. The metal salt containing composite looks similar to pure PANI, leading to the assumption that the metal ions build an intercalation compound with the polymer. The metal oxide containing composite confirms the assumption that PANI is adsorbed at the Nb₂O₅ particles. The TEM images in Fig. 3 illustrate a difference between the two samples prepared by adding the Nb₂O₅ before or after starting of the polymerisation respectively. Adding Nb₂O₅ to the solution before the start of polymerisation results in the adsorption of monomers to Nb₂O₅ and start of polymerisation at every single Nb₂O₅ particle, which is encased than by pure, crystalline PANI. Contrary to that the admixture of Nb₂O₅ after starting the polymerisation results in the randomised adsorption of polymeric macromolecules to the oxide particles, which are not completely encased after this procedure.

The grain sizes of the different composites differ with a particle size distribution around 0.5 μm for the metal oxide containing composites to 1.1 μm for the metal salt containing composite. For comparison, the size distribution of pure PANI is about 1.2 μm.

3.2. Thermal behaviour

As it is well known from the literature adequate thermal stability of the pure PANI is limited to temperatures below 250 °C which is outside the range of working temperatures of YSZ based solid electrolyte sensors between 450 ... 800 °C. The thermogravimetric investigation given in Fig. 4a shows, that pure PANI loses more than 90% of its weight at the temperature 500 °C. The cracking products of the PANI pyrolysis could not be characterised. According to [18] the thermal decomposition can result in several carbazoles, aminocarbazoles, phenylamines and other intermediates. According to Fig. 4b the thermal behaviour of the polymer

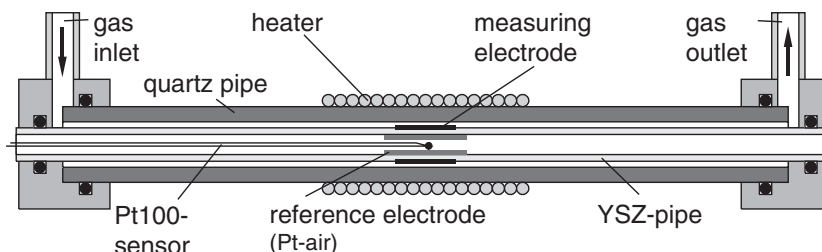


Fig. 2. Setup of YSZ cell with conducting polymer electrodes for potentiometric measurements.

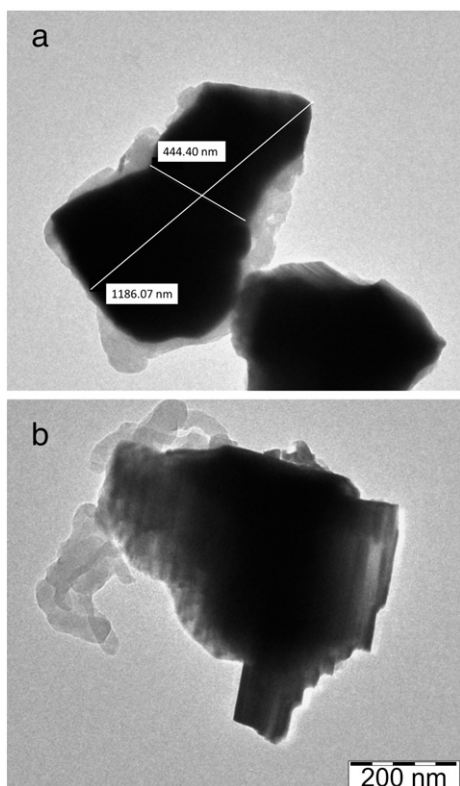


Fig. 3. TEM images of Nb₂O₅ containing PANI composites. a) Nb₂O₅ is added before starting the polymerisation. b) Nb₂O₅ is added after starting the polymerisation.

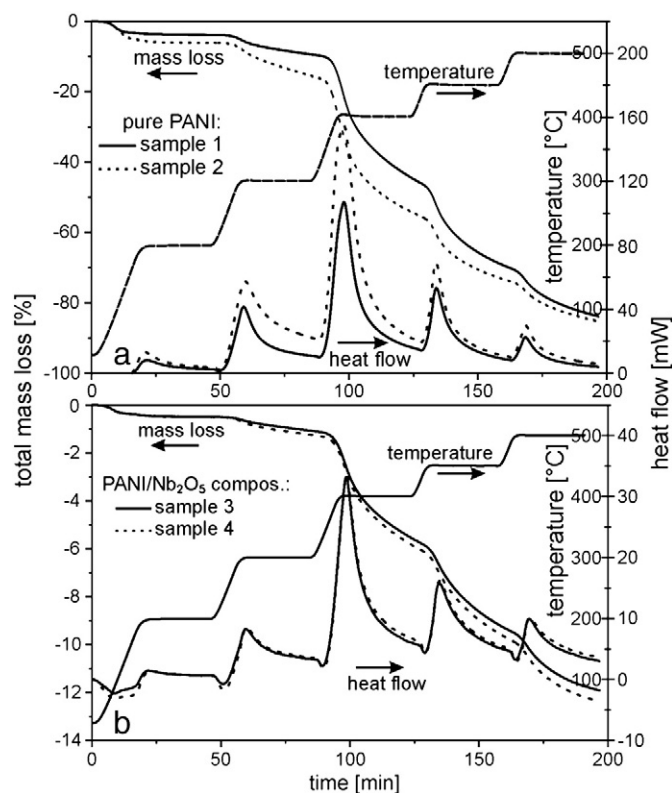


Fig. 4. Thermal characterization curves of pure PANI (4a) and its Nb₂O₅ containing composites (4b), sample 1: pure PANI with 0.1 mol aniline in 1 l 1 N HCl, sample 2: preparation acc. to [10], sample 3: Nb₂O₅ added before start of polymerization, sample 4: Nb₂O₅ added after start of polymerization.

can be influenced by the formation of a composite. The added metal oxide Nb₂O₅ increases the thermal stability significantly, resulting in the reduced weight loss 12% at 500 °C.

Related to the amount of pure PANI in the PANI/Nb₂O₅ composite (2:1 molar mixing ratio), the weight loss at 500 °C can be calculated by the following equation:

$$\text{PANI mass loss in composite} = \left(2 \cdot M_{\text{PANI}} + M_{\text{Nb}_2\text{O}_5}\right) \cdot \frac{12\%}{2 \cdot M_{\text{PANI}}} = 29\%.$$

As it can also be seen from Fig. 4, the composite with metal oxide added before starting the polymerisation shows a slightly higher thermal stability than the composite with Nb₂O₅ added after start of polymerisation. One reason of that lower thermal stability might be related to the incomplete covering of the grains with PANI.

Also the more acidic composite shows that pronounced effect of thermal stabilisation, revealing that the pH value of the composite does not influence the thermal behaviour of the Nb₂O₅ containing CPC. In contrast to that the composite with the incorporated metal salt ions exhibits nearly the same thermal behaviour like pure PANI resulting in more than 90% pyrolysed composite at 500 °C.

The reasons for thermal stabilisation could not be clarified, so far. One approach to be followed in future research consists in examining the reactive chain ends of the polymer, occurring by heating the mixture. These reactive ends might bind to the metal oxide and stabilise the composite, which might result in the observed colour change. Due to the fact that pure PANI as well as the FeCl₃/Co(NO₃)₂ containing composite did not change their colours after the thermal treatment it can be concluded that a large amount of pure polymer remained in the thermally treated samples. The metal oxide containing composites have been changed their colours from blue/white to grey/white, but it could not be clarified, why the polymer colour disappeared, although it was verified that PANI remains in the composite.

3.3. Catalytic behaviour and conductivity

Catalytic activities of electrode materials for the oxidation of the gaseous components to be measured with mixed potential sensors influence their sensitivity and gas consumption significantly [19]. This complementary investigation is therefore carried out to screen promising electrode materials. Fig. 5 shows significant differences between the investigated materials. The composites with acidic character show higher catalytic activities than the ones prepared by intensive washing with end pH value = 4. Conductivity measurements at pressed powder

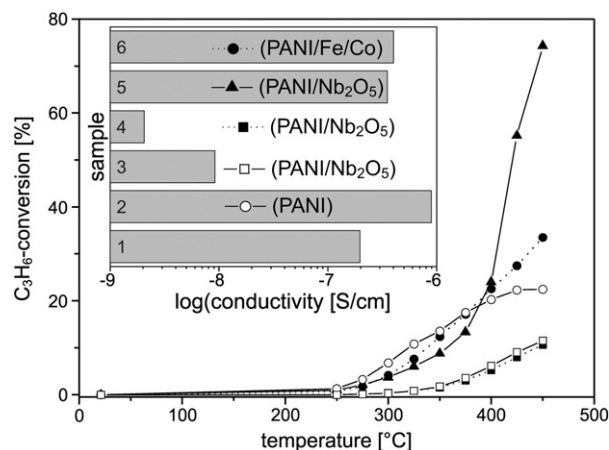


Fig. 5. Catalytic activity of investigated materials to propene conversion, inset: conductivity of pressed powders, sample 1–4 see Fig. 4, sample 5 Nb₂O₅ CPC washed till colour change of precipitate, sample 6: PANI with FeCl₃/Co(NO₃)₂.

samples (see inset in Fig. 5) show correlations to the results of catalytic activity. As expected the acidic composites exhibit higher conductivities than the intensively washed composites due to their much higher concentration of remaining highly conductive protons. Therefore, acidity is necessary to provide sufficient electrode conductivity and to enable appropriate charge transfer, which is required for the adjustment of the mixed potential.

3.4. Potentiometric investigation

Electrodes made from the samples with pure PANI, the composites with Nb_2O_5 , washed till pH = 4 and pure Nb_2O_5 -electrodes show no measurable sensitivities in the investigated gas mixtures. In contrast to that the potentiometric investigations indicate comparably high sensitivities for the more acidic PANI composites as given in Fig. 6.

While the metal oxides and salts in the composites are responsible for oxygen exchange with the gas phase and the solid electrolyte, catalytic behaviour and thermal stabilisation, the PANI in the composites plays an important role for electrode conductivity. The interactions between niobium oxide and polyaniline may reflect their chemical identities. If the acidity is not too strong, anionic niobate may exist at the interface with positively charged PANI species. The ratio of the composite mixture results from an optimization procedure described elsewhere [20].

The results of the $\text{FeCl}_3/\text{Co}(\text{NO}_3)_2/\text{PANI}$ -electrode (FCP-electrode) show that the logarithmic response expected from the mixed potential theory [3] is established at concentrations above 100 vol.ppm in the case of H_2 , 50 ppm for C_3H_6 and 10 ppm for C_2H_4 . The limit of detection

is not reached within the investigated concentration range of every combustible. At the concentrations 10 vol.ppm (H_2 and C_3H_6) and 1 vol.ppm (C_2H_4) the sensitivities range between 0.6 ... 8.5 mV/vol.ppm. The maximum sensitivity found at FCP-electrode in ethene containing mixture is much higher than those obtained for mixed oxide electrodes. The comparison of different sensitivities in Fig. 6b with the curves of catalytic conversion in Fig. 5 proves that higher sensitivities of the investigated CPC samples do not correlate with lower catalytic activities, but that the sensitivity increases with conductivity. The comparison between two electrodes made of the same CPC but different binders confirms that this additive has also a pronounced influence on the potentiometric behaviour. Due to the very low firing temperatures the commercial binder from ESL seems to provide additional combustibles over a prolonged period of measurement, while the cellulose acetate based binder vanishes nearly completely during the preparation process.

The electrode measurements could be repeated more than 10 times with a sensitivity decrease below 10%, indicating sufficient reproducibility of newly prepared sensors. After longer operation periods elevated sensitivity decrease reveals ageing processes, which could be related to a limited mechanical stability of the printed electrode layers. This disadvantage could not be solved yet and will be addressed intensively in future investigations.

4. Conclusions

New composite materials based on the simple and cost effective conductive polymer polyaniline (PANI) have been prepared and tested successfully as mixed potential electrodes of YSZ based solid electrolyte sensors in hydrogen and hydrocarbons (C_3H_6 and C_2H_4) at 450 °C for the first time. Different types of synthesised PANI composites, containing Nb_2O_5 or FeCl_3 and $\text{Co}(\text{NO}_3)_2$, showed enhanced conductivity and simultaneously enhanced sensitivity by reclaiming the materials very acidic. These sensitivities are much higher than those measured at the intensively investigated composites of metals (gold) and oxides (i.e. Ta_2O_5). The measured sensitivities do not correlate with the catalytic behaviour of the composites due to large differences of the specific conductivities.

The metal oxide containing composites build agglomerated core shell compounds with completely coated PANI layers around the Nb_2O_5 grains, when adding the Nb_2O_5 before starting the polymerisation. The implementation of Nb_2O_5 causes remarkable thermal stabilisation of the conductive polymer composites, while the reasons for that behaviour are not clarified, yet. The metal salt containing composite, building an intercalation compound, does not show any stabilisation effects, but elevated sensitivity in potentiometric investigations. The synthesised materials exhibit reproducible mixed potential signals in dependence on concentration of combustibles at 450 °C over several days, but limited mechanical stability leads to rapid ageing. Beside further investigations on electrode materials and their structure and composition by introducing other conductive polymers, metal oxides and by variation of preparation parameters, the improvement of the mechanical stability will be addressed preferentially.

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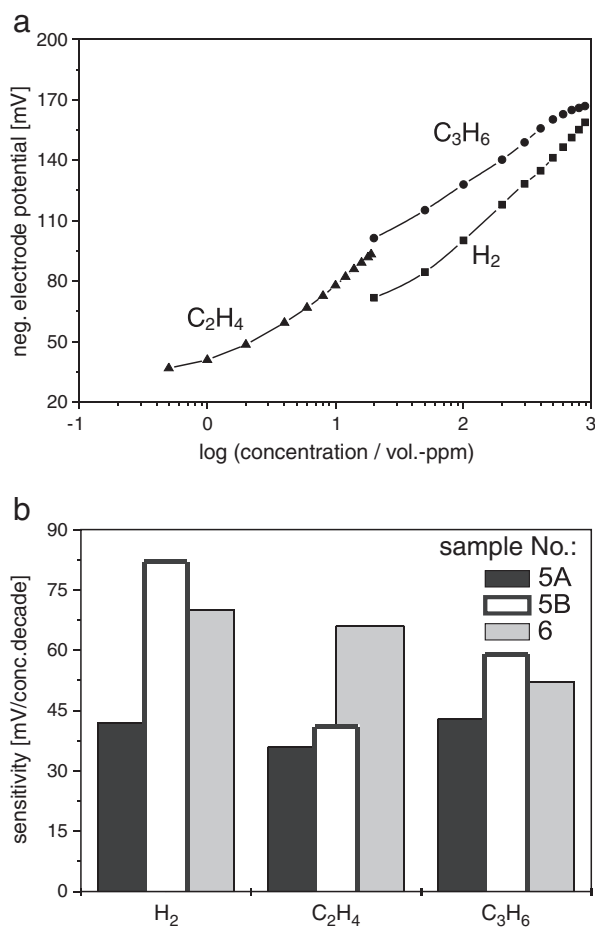


Fig. 6. Potentiometric response for H_2 , C_3H_6 and C_2H_4 of the acidic polymer composite sample 6 (a) and comparison of sensitivities of the sample 5, prepared with the commercial ESL binder (sample 5A) and the cellulose acetate binder (sample 5B) and sample 6 (b).

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