INTERFACE REACTIONS AMONG ELECTRODES, SUBSTRATES AND Pb(Zr,Ti)O_3-BASED FILMS[†]

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[†]This paper is dedicated to the late Professor dr. Drago Kolar

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Abstract

Interactions between (Pb,La)(Zr,Ti)O_3 (PLZT) thin and thick films and silicon or alumina substrates, respectively, were studied. In the case of thin films the lowering of the firing temperature inhibits the formation of secondary phases. For thick films the additional layer of PLZT between the alumina substrate and the Pt electrode improves adhesion within the PLZT thick-film heterostructures. Interactions between conductive oxides which could be used as electrodes instead of noble metals and PZT-based materials are reported.

Key words: ferrolectric ceramics, interactions, heterostructrure, films, conductive oxides

Introduction

Ferroelectric (FE) materials are frequently based on solid solutions of Pb(Zr,Ti)O_3 (PZT) or La-doped (Pb,La)(Zr,Ti)O_3 (PLZT). Ferroelectric films are good candidates for a number of applications including nonvolatile memories (ferroelectric random-access memory, FRAM), microsensors, microactuators and printing elements.[1-3] Most current investigations in this field are aimed at the development and characterisation of ferroelectric thin films where the typical thicknesses range from a few 10 to 1000 nm.

Among the various deposition methods for FE thin films, chemical solution deposition methods (CSD) have received considerable attention because of their many advantages including simple processing, coverage of large areas and good control of stoichiometry.[1,2] The first step in CSD is the synthesis of a stable multicomponent precursor solution. The integration of ferroelectric thin films into devices requires deposition of the precursor onto an electrode (typically Pt) in contact with Si and a post-depositional heat treatment at elevated temperatures. Typically, thicknesses between 50 and 300 nm are obtained by this procedure. The perovskite crystallization temperatures of PZT thin films are between 500 °C and 650 °C. The heat treatment often causes interdiffusion, especially of Si and Pb, through the commonly used Pt electrode, which is between the PZT or PLZT film and the substrate.[4-6] This interdiffusion and lead-oxide evaporation [7] during the heat treatment are detrimental to the formation of the perovskite phase and leads to the formation of a lead-deficient surface pyrochlore-type phase, which critically decreases the functional response of the thin films. Both processes may be limited by lowering the crystallization temperature. Heat-treatment temperatures needed for complete crystallization can be significantly lowered by the use of nucleation layers, such as $PbTiO_3$ in the case of PZT-based thin films.[4]

For some piezoelectric applications, e.g. micro-actuators or micro-levers, an increased thickness is required.[8] This can be achieved by repeating the deposition heat-treatment steps almost ad infinitum however both the reaction of the film with the substrate and the lead-oxide surface evaporation become more important with an increased number of iterations and therefore the functional response of the film deteriorates. High-quality films thicker than a few micrometers have not been achieved with CSD.[9,10]

Thick-film technology, i.e. the deposition of thick-film pastes by screen printing mainly on alumina substrates, is a relatively simple and convenient method to produce thicker layers with thicknesses from a few μm up to 100 μm. The characteristics of thick-film ferroelectrics are similar to those of bulk materials. However, thick films are processed at higher temperatures than thin films, thus increasing the possibility of interactions either with the electrodes or substrates and a consequent degradation of the film characteristics.

Data in the literature indicate that some characteristics of PZT films can be improved with the use of either $LaCoO_3$-, $LaNiO_3$- or RuO_2-based conductive oxides for electrodes instead of Pt electrodes.[11-15] The published results are reported mainly for thin-film structures, where the highest annealing temperatures are limited to relatively low values, up to 600 °C-700 °C, and the possible interactions on the conductive oxide/PZT interface do not proceed to any significant extent.

In this paper the studies of the interactions between thin and thick films with Si and Al_2O_3 substrates, respectively, and interactions among conductive oxides ($LaNi_{0.6}Co_{0.4}O_3$, $SrRuO_3$ and RuO_2) with PZT-based materials will be presented.

Experimental

Thin-film processing

The PLZT 9,5/65/35 composition was selected. The generally accepted compositional notation is used, where PLZT x/y/z represents composition with x at % La instead of Pb and y/z represents the Zr/Ti ratio. The chemical composition is based on charge compensation by introducing vacancies on the A site ($Pb_{1-3x/2}La_xZr_{0,65}Ti_{0,35}O_3$). 10 % of PbO excess is added to the stoichiometric composition in order to compensate for PbO evaporation upon thermal treatment. The PLZT sols were prepared from Pb acetate hydrate, La acetate hydrate, Ti n-propoxide and Zr n-propoxide in 2-methoxyethanol (MEO) as a common solvent. Acetates were dried prior use. The flow chart of the PLZT sol syntheses via the methoxyethanol route is shown in Figure 1.

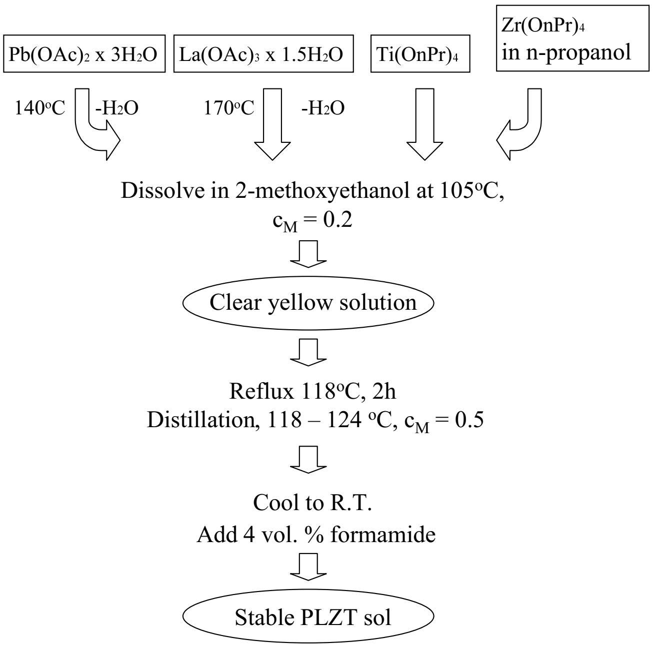

Fig. 1: The flow chart of the PLZT sol synthesis via the methoxyethanol route.

$PbTiO_3$ nucleation layers were prepared from anhydrous lead acetate and titanium n-propoxide in 2-methoxyethanol by a similar procedure to that shown in Figure 1 and deposited by spin coating (3000 rpm for 60 seconds) on Pt/TiO_2 sputtered silicon substrates. Single layers from sols of 0.0625M were deposited. The deposition was followed by pyrolysis (350 °C, 60 sec.) and by thermal treatment at 500 °C to obtain crystallized $PbTiO_3$ layers. PLZT sols were subsequently deposited on the as prepared substrates. Thin films consisted of typically 5 layers to obtain a final thickness in the range 300 - 500 nm. The films were pyrolyzed at 350 °C for 60 sec. and then heat treated in air at temperatures from 400 °C to 600 °C.

Thick- film processing

PLZT ($Pb_{0,88}La_{0,08}Zr_{0,65}Ti_{0,35}O_3$) with 6 mole.% excess PbO and PZT with the composition $Pb(Ti_{0.5}Zr_{0.5})O_3$, were synthesised from PbO (litharge, 99.9%, Fluka), ZrO_2 (99%, Tosoh), TiO_2 (99 % Fluka) and $La(OH)_3$. The mixture of starting chemicals was fired twice for 2 hours at 900 °C with intermediate grinding and milling in a zirconia mill with acetone. According to X-ray powder-diffraction analyses (XRD), PLZT and PZT solid-solution formation was achieved during synthesis. A thick-film paste was prepared from the synthesised powders and an organic vehicle by mixing them in a three-roll mill. Demetron platinum paste without glass phase, type 410, was screen printed as a bottom electrode on the Al_2O_3 substrates and fired at 1400 °C for 2 hours. On the fired Pt electrode a PLZT layer was screen printed and sintered at 1100°C for up to 8 hours in a PbO-rich atmosphere within a closed alumina crucible. The source of PbO was a $PbZrO_3$/PbO powder.

Interactions between conductive oxides and PZT-based perovskites

Material with the nominal composition $LaNi_{0.6}Co_{0.4}O_3$ was prepared by coprecipitation of hydroxides. After washing and drying the material was calcinated at 850 °C for 24 hours (for more details see [16]). $SrRuO_3$ was synthesized from stoichiometric mixtures of $SrCO_3$ (Ventron, 99.9%) and RuO_2 (Ventron, 99.9%). The oxide and the carbonate were mixed in isopropyl alcohol, pressed into pellets, calcined at 1000 °C and fired at 1200 °C for 50 hours with intermediate grinding. During firing the pellets were placed on platinum foils. Possible interactions between conductive oxides and PZT-based materials were studied by firing powder mixtures for 2 hours at different temperatures.

Characterization

The samples were analysed by XRD with a Philips PW 1710 X-ray diffractometer using CuK_α radiation. X-ray spectra were collected from $2\Theta = 15\text{-}65^o$ in steps of 0.02^o. A JEOL JMS-5800 scanning electron microscope (SEM) equipped with a LINK ISIS 300 energy-dispersive X-ray analyser (EDX) was used for overall microstructural and compositional analysis. Prior to analysis in the SEM, the sample was coated with carbon to provide electrical conductivity and prevent charging effects. Cross-section samples of thin films were characterized by transmission electron microscopy (Jeol 2000 FX TEM). The adhesion between the electrodes, substrates and thick-film active layer was evaluated by the Scotch-tape method. Self-adhesive tape was fixed on the film and then sharply peeled off.

Results and discussion

Thin films

The crystallization of PLZT 9,5/65/35 films heated at different temperatures was followed by XRD analysis. The results are summarised in Table 1. The perovskite phase is formed after 10 minutes at 800 °C, however, at this temperature the problem of lead-oxide evaporation from the thin-film surface is enhanced. At lower temperatures, longer heating times are required.

Table 1: Phase composition of 9,5/65/35 PLZT films, deposited on layer of lead titanate and platinum, determined by XRD.
Per: perovskite, Py: pyrochlore-type phase

Temperature [^{o}C]	Time	Phase composition
800	10 min	Per
700	10 min	Per, Py
700	60 min	Per, Py
700	90 min	Per
600	20 hours	Per
550	20 hours	Per
400	65 hours	Per

Cross-section TEM analysis of PLZT 9,5/65/35 film heated for 20 hours at 600 ^{o}C (Fig. 2) revealed that the perovskite phase nucleates on a $PbTiO_3$ nucleation layer and grows with a columnar morphology.

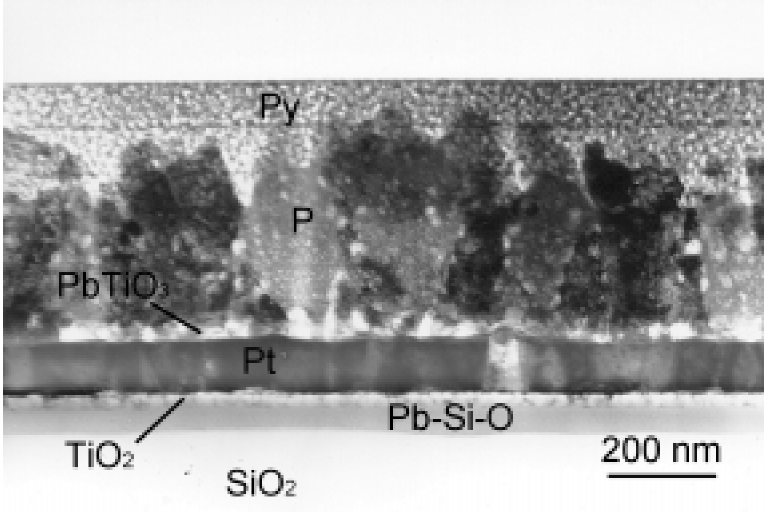

Fig. 2: Cross-section TEM micrograph of PLZT thin film on $Si/SiO_2/TiO_2/Pt$ substrate with the $PbTiO_3$ nucleation layer after annealing at 600 °C for 20 h. P: perovskite, Py: pyrochlore-type phase.

The surface of the film is a fine-grained pyrochlore. Note, however that the pyrochlore-type phase was not detected by XRD. An amorphous layer of lead silicate was found beneath the platinum electrode, indicating a reaction between lead and silicon oxides. A plausible explanation for the glassy layer is the presence of defects (holes) in the platinum, enabling the reaction upon thermal treatment.[6] The presence of the pyrochlore is either due to noncomplete transformation of the pyrochlore or to PbO losses either prior to crystallisation or from already-formed perovskite by evaporation and/or due to the reaction with the substrate during the long heating time.

Cross section TEM analysis of the PLZT 9,5/65/35 film heated for 65 hours at 400°C (Fig. 3) revealed the columnar growth of the perovskite phase on a $PbTiO_3$ nucleation layer. The rather low heat-treatment temperature was chosen in order to minimize lead-oxide evaporation and to avoid the interaction between the film and the substrate. According to the literature data, lead-silicate glassy phase was detected at temperatures above 500 °C.[6] The presence of the pyrochlore-type phase was not detected.

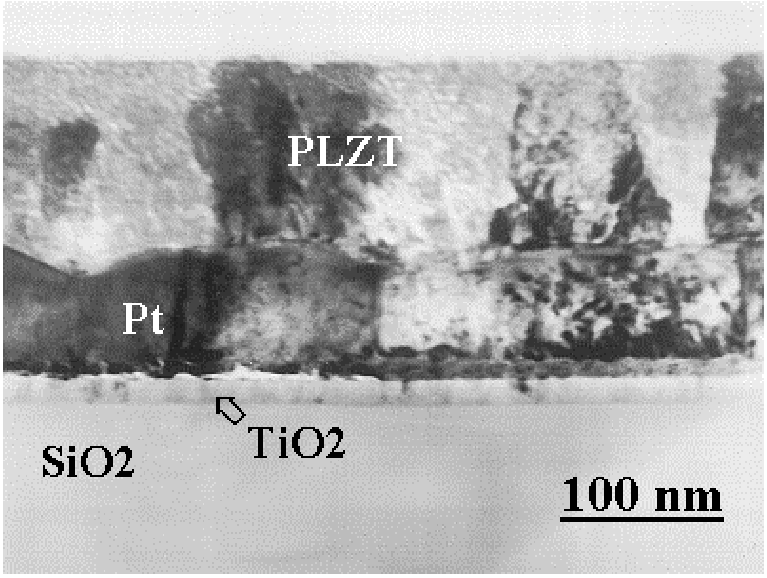

Fig. 3: Cross-section TEM micrograph of PLZT thin film on Si/SiO_2/TiO_2/Pt substrate with the $PbTiO_3$ nucleation layer after annealing at 400 °C for 65 h.

Interactions between PLZT thick film and alumina substrate

The adhesion of the Pt/PLZT layer after firing at 1100 °C was very low; it was easily peeled off the alumina substrate with Scotch tape. In the remainder of the text the surface of the substrate which was covered by the Pt layer will be denoted “surface A”, and the lower surface of the peeled off platinum layer as “surface B”.

The adhesion of the platinum layer, which was not over-printed with PLZT film, was good; it could not be peeled off with the Scotch-tape test. The results indicate that the adhesion of the platinum film to the alumina substrate decreased significantly due to firing the PLZT film on the Pt electrode. Surface A (alumina substrate) from which the Pt/PLZT layer was peeled off, is shown in Fig. 4. Relatively large crystals of secondary phase were observed on the surface. According to an EDX analysis the main elements detected were aluminum (35.6 at.%), lead (2 at.%) and lanthanum (1.5 at.%), with minor concentrations of titanium, calcium and magnesium (less than 0.5 at.%). Lead, lanthanum, and titanium were incorporated from the PLZT layer, while calcium and magnesium originated from the impurities in the substrate.

The lower surface of the peeled-off platinum electrode, i.e. surface B, which was in contact with the alumina, is shown in Fig. 5. The Pt film is densely sintered with a few small pores through which the PLZT layer can be observed. The platinum is also covered with hexagonal crystals of secondary phase. EDX analysis showed the presence of the same elements as in the secondary phase on the alumina substrate.

The XRD spectrum of surface B (the peeled-off platinum electrode) shows, besides Pt peaks, peaks of the hexagonal compound $PbAl_{12}O_{19}$ with a β-Al_2O_3 structure (JCPDS-20-558). It is interesting to note that the $PbAl_{12}O_{19}$ compound cannot be prepared from "pure" PbO and Al_2O_3.[17] The results indicate that doping with La_2O_3 from the PLZT or impurities from the alumina substrate stabilises the β-Al_2O_3 type compound. This is in agreement with the results of Comer at al.[18], who reported that the addition of small amounts of rare-earth activator ions must be used for the successful synthesis of $PbAl_{12}O_{19}$.

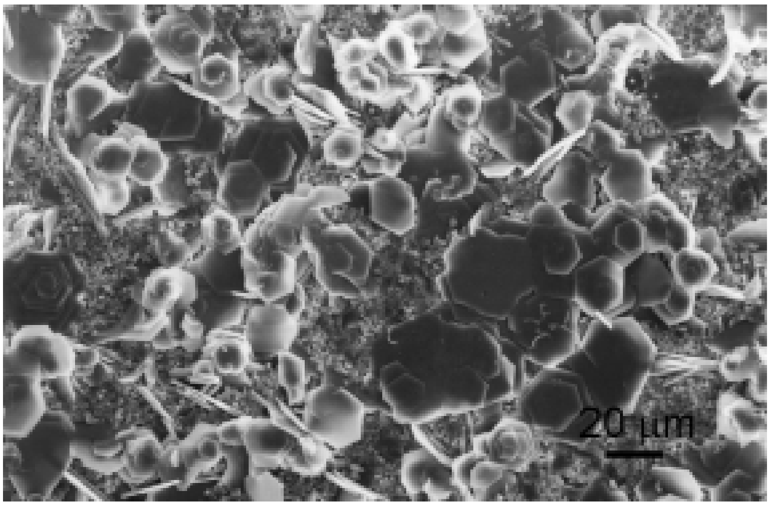

Fig. 4. The microstructure of surface A – the alumina substrate with hexagonal $PbAl_{12}O_{19}$ crystals.

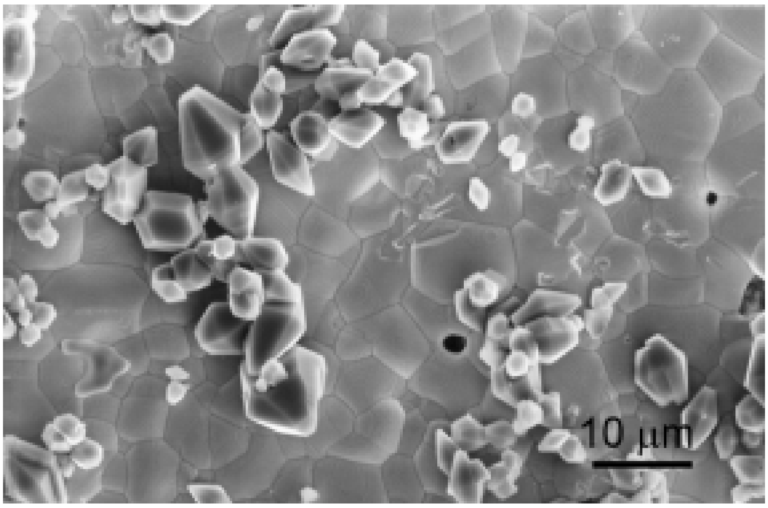

Fig 5. The microstructure of surface B – platinum electrode with $PbAl_{12}O_{19}$ crystals.

The low adhesion of the platinum layer to the alumina substrate, after the PLZT layer is fired, is therefore attributed to the formation of crystals of a $PbAl_{12}O_{19}$-type compound. PbO forms low-temperature eutectics with La_2O_3 [19] at 770 °C and with TiO_2 [20,21] at 838 °C. During firing the PbO-rich liquid phase is transported through pores in the platinum electrode layer and reacts with Al_2O_3. However, as mentioned before, some other oxide must be present to activate the reaction. The crystals were “pushed off” the platinum electrode from the substrate, resulting in very low adhesion. The problem was successfully overcome with an additional layer of PLZT, printed and fired between the alumina substrate and the Pt electrode.[22,23]

Interactions between conductive oxides and PZT-based perovskites

Results of the X-ray powder-diffraction analysis of the fired mixtures of conductive oxides and PZT-based materials are summarised in Table 2.

Both conductive perovskites, i.e. $LaNi_{0.6}Co_{0.4}O_3$ and $SrRuO_3$, react with the PLZT. The quantity of reacted products increases with increasing firing temperature. The reactions of the perovskites with the PLZT resulted in the perovskite solid solutions incorporating ions from the conducting perovskites into the PLZT structure. In the case of $LaNi_{0.6}Co_{0.4}O_3$ even after firing at 1000 °C the conductive perovskite “decomposed” completely resulting in $La_2Zr_2O_7$, PLZT solid solution and PbO. For $SrRuO_3$,

$Pb_2Ru_2O_{6.5}$ was one of the reaction products. RuO_2 also reacts with PZT forming $Pb_2Ru_2O_{6.5}$.

Table 2: X-ray powder diffraction analysis of powder mixtures, fired for 2 hours at different temperatures.

Powder mixture	Temp [^{o}C]	Phases identified
$SrRuO_3$ + PLZT	1000	$SrRuO_3$, (La,Pb,Sr)(Zr,Ti,Ru)O_3 ss, $Pb_2Ru_2O_{6.5}$
	1100	$SrRuO_3$, (La,Pb,Sr)(Zr,Ti,Ru)O_3 ss, $Pb_2Ru_2O_{6.5}$
	1200	$SrRuO_3$, (La,Pb,Sr)(Zr,Ti,Ru)O_3 ss, $Pb_2Ru_2O_{6.5}$
$LaNi_{0.6}Co_{0.4}O_3$ + PLZT	1000	$La_2Zr_2O_7$, (La,Pb)(Ni,Zr,Ti,Co)O_3 ss, PbO
	1100	$La_2Zr_2O_7$, (La,Pb)(Ni,Zr,Ti,Co)O_3 ss, PbO
	1200	$La_2Zr_2O_7$, (La,Pb)(Ni,Zr,Ti,Co)O_3 ss, PbO
RuO_2 + PZT	950	RuO_2, PZT, $Pb_2Ru_2O_{6.5}$

ss - solid solution

While the data in the literature show the successful application of conductive perovskites and RuO_2 for bottom electrodes for thin-film structures the results, summarised in Table 1, indicate that, due to interactions with PZT-based perovskites, they cannot be used for thick-film structures. The main reason is the higher firing temperature required for thick films. However, the phase equilibria in the systems relevant to the possible interactions between PZT and RuO_2 indicate that $Pb_2Ru_2O_{6.5}$ (which is also formed as a result of reactions between RuO_2 or $SrRuO_3$ and PZT-based materials), would be a useable electrode material.[24] Preliminary results on the compatibility of $Pb_2Ru_2O_{6.5}$ and PZT confirm these conclusions.

Conclusions

Interactions between PLZT thin and thick films and silicon or alumina substrates, respectively were studied. Diffusion of lead oxide into the silicon substrate in the case of thin films induces the formation of a glassy phase below the Pt electrode. The consequent loss of stoichiometry of the perovskite phase results in the formation of a nonferroelectric pyrochlore phase. Lowering the temperature of annealing from 600 °C to 400 °C inhibits the pyrochlore formation.

In the case of thick films the transport of lead and lanthanum oxide through the platinum electrode to the alumina substrate induces the formation of secondary phases and causes the deterioration of adhesion. The problem was overcome with an additional layer of PLZT between the alumina substrate and the Pt electrode.

Conductive oxides are in some applications, possible replacements for electrodes based on noble metals. The interactions between PZT-based materials and electrode candidates, such as $LaNi_{0.6}Co_{0.4}O_3$, $SrRuO_3$ or RuO_2 were investigated. Preliminary results show the formation of secondary phases after firing in the temperature range from 950 °C to 1200 °C and which indicates the incompatibility of the chosen combinations. Lead ruthanate, formed as a result of reactions between RuO_2 or $SrRuO_3$ and PZT-based materials, would be a useable electrode material.

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Povzetek

Študirali smo reakcije med tankimi in debelimi PLZT plastmi na silicijevih in korundnih podlagah. Pri tankih plasteh preprečimo nastanke sekundarnih faz z nižjo temperaturo žganja. V primeru debelih plasti pa z nanosom vmesne plasti med elektrodo in podlago izboljšamo mehanske oprijemljivost med platinsko elektrodo in podlago. Prevodne okside lahko uporabljamo namesto kovinskih elektrod. V delu poročamo o reakcijah med materiali na osnovi PZT in vrsto prevodnih oksidov.