

## Alternative Processes for Manufacturing of Metal Oxide-based Potentiometric Chemosensors

<sup>1</sup> Winfried VONAU, <sup>1</sup> Manfred DECKER, <sup>1</sup> Jens ZOSEL,  
<sup>1</sup> Kristina AHLBORN, <sup>1</sup> Frank GERLACH, <sup>2</sup> David HALDAN  
and <sup>2</sup> Steffen WEISSMANTEL

<sup>1</sup> Kurt-Schwabe-Institut für Mess- und Sensortechnik,  
Kurt-Schwabe-Straße 4, 04736 Waldheim, Germany  
<sup>2</sup> Hochschule Mittweida, Fakultät Ingenieurwissenschaften,  
Technikumplatz 17, 09648 Mittweida, Germany  
<sup>1</sup> Tel.: +49 34327 608 0, fax: +49 34327 608131  
<sup>1</sup> E-mail: [info@ksi-meinsberg.de](mailto:info@ksi-meinsberg.de)

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**Abstract:** New possibilities for the preparation of partially selective redox electrodes based on passivated metals of the subgroups IV to VI of the periodic system are presented by the example of vanadium. The gas phase oxidation at controlled oxygen partial pressures (CPO) and the pulsed laser deposition (PLD) as an high-vacuum method are utilised as alternative methods beside the well-established chemical and electrochemical passivation which usually lead to the highest possible oxidation state of the passivated metal. These newly available methods enable in principle the tailoring of oxidation states in the sensitive layer and therefore the optimisation of the electrochemical sensitivity and selectivity of sensors equipped with it. The use of vanadium as basic electrode material is crucial because it shows in several matrices a remarkable corrosion susceptibility. This problem can be solved by the introduction of stable alloys with high vanadium contents. These materials can be efficiently produced by pulsed laser deposition (PLD). *Copyright © 2015 IFSA Publishing, S. L.*

**Keywords:** Partial selective redox electrode, Chemical passivation, Electrochemical passivation, Gas phase oxidation, Pulsed laser deposition.

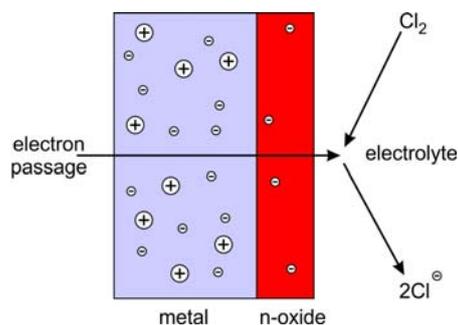
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### 1. Introduction

Measurements of the oxidation/reduction potential (ORP) are suited for online determination of oxidising agents like halogens or hydrogen peroxide e.g. in process and waste waters, if the electrode materials provide a partial selectivity [1]. It is already known that systems made of passivated metals of high purity

(> 99.5 wt.-%) of the subgroups IV to VI of the periodic system are suited for this purpose. The favourable sensory behaviour is related to the semiconducting and corrosion properties of the oxide layers with electronic and ionic defects. Investigations have shown that for the quality of the sensor functionality an n-type conducting mechanism is favourable, accordingly the passivating sensing oxide should be an n-type semiconductor. The sensor is working like a Schottky-diode

[2]. Fig. 1 presents in this context exemplarily the electrochemical process for a chlorine determination at a passivated titanium electrode.



**Fig. 1.** Electron migration at a titanium/ titanium oxide electrode.

The preparation of the oxide layers was carried out so far by chemical passivation [M(ethod) 1)] using air or pure oxygen as oxidising agent or by anodic oxidation [M 2)] in half concentrated acids (e.g. sulfuric and nitric acid) [3], leading usually to the highest possible valence state of the metal at the outer electrode surface. The inner oxide layer near the metal bulk can contain also lower valence states.

In Table 1, appropriate metals for the construction of potentiometric sensors with partial selectivity versus selected analytes are presented. Fig. 2 shows a possible design for the described electrode according to the state of the art.

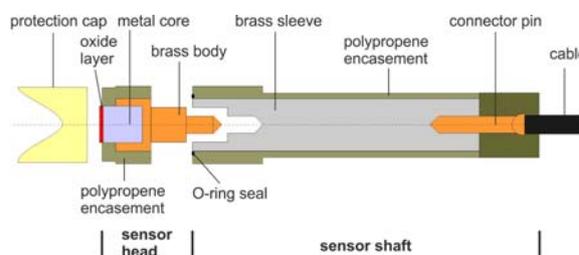
**Table 1.** Membrane materials for the fabrication of partial selective electrodes.

analyte in aqueous phase	electrode material				
	Ti	Ta	W	Nb	V
Cl <sub>2</sub>	x	x	x		
Br <sub>2</sub>	x	x	x	x	
I <sub>2</sub>			x		
NO <sub>2</sub> <sup>-</sup>			x		
H <sub>2</sub> O <sub>2</sub>					x
Fe <sup>3+</sup>	x				

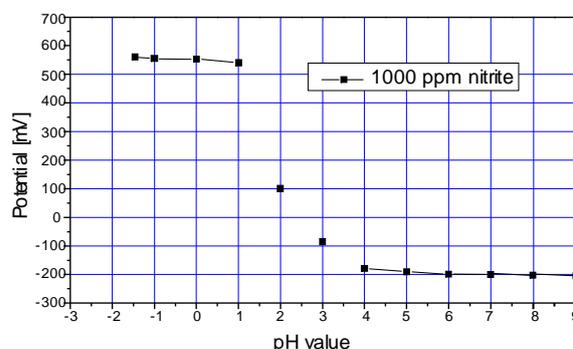
Generally, electrodes made of these materials exhibit a cross sensitivity to the pH value which should be known and considered. As an example for such a behaviour Fig. 3 shows results for the determination of nitrite by means of an anodically passivated tungsten based indicator electrode (according to Fig. 2) at pH values between -1.4 ... 9. There are two ranges with negligible influence of the pH value on the nitrite concentration related electrode potential (range 1: pH= -1.4 ... 1; range 2: pH= 4 ... 9). Therefore, a simultaneous pH determination is always advantageous, whereupon the existing problems of pH measurement

with glass based or other pH electrodes in strong acidic media should be considered.

To tailor the most important parameters sensitivity and selectivity of the described partial selective electrochemical sensors it might be advantageous to prepare oxide layers in contact with the electrolyte which also possess several lower oxidation states with sufficient chemical stability.



**Fig. 2.** Redox electrode with passivated metal disk as partial selective membrane.



**Fig. 3.** Nitrite determination with tungsten oxide electrodes vs. Ag/AgCl, Cl<sup>-</sup><sub>sat</sub>.

In this connection in section 2, the preparation, characterisation and application of membrane materials for partial selective electrodes based on passivated pure metals of subgroups IV-VI is described exemplarily by using vanadium as source material. Here, the final goal was to develop a potentiometric electrode for the determination of H<sub>2</sub>O<sub>2</sub> in process-relevant applications. In addition to the known use of M 1 and M 2 for this purpose electrode preparations also were carried out by means of gas phase oxidation at controlled temperature and oxygen partial pressure [CPO (M 3)] and pulsed laser deposition [PLD (M 4)].

Based on the knowledge gained during the first potentiometric sensory applications of these novel materials in section 3 new perspectives are presented. The innovative production technologies allow a cost- and material-saving manufacturing of tailored passivated electrodes on the base of alloys of the above-mentioned subgroup metals. This has particular relevance for the fabrication of vanadium oxide electrodes which show remarkable corrosion in aggressive media resulting in a reduced service life.

## 2. Electrode Preparation, Characterisation and Application

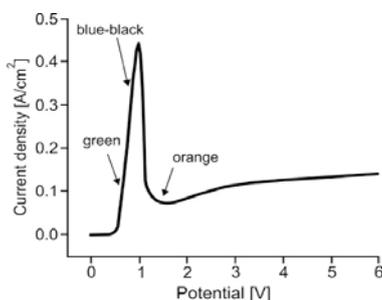
### 2.1. Preparation

#### M 1

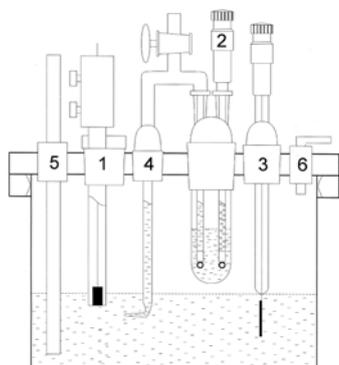
Vanadium disks were fabricated from a metal bar (purity: 99.8 wt.-%,  $\varnothing$ : 1 cm) using a diamond saw, contacted with a Pt-wire, encased by an insulating polymer (e.g. polypropylene) and wet grinded with sandpaper (grain size: 4000). After cleaning of the metal surface by back sputtering passivation was carried out using air or pure oxygen (low content of carbon dioxide and water vapour) as oxidising agent at temperatures  $< 100\text{ }^\circ\text{C}$ .

#### M 2

Fig. 4 shows the electrochemical polarisation curve of a high-purity vanadium disk (prepared as described before) in sulfuric acid obtained within the range of  $U_P = 0 \dots 6\text{ V}$  vs.  $\text{Ag}/\text{AgCl}$ ,  $\text{Cl}^-_{(\text{sat.})}$  at the scan rate  $100\text{ mV/s}$  which was recorded in the course of the production of a related partial selective electrode. The observed colour changes of the vanadium surface seem to be in correlation with the formation of  $\text{VO}$  (green),  $\text{VO}_2$  (blue-black) and  $\text{V}_2\text{O}_5$  (orange) as the final state. The anodic oxidation process was carried out using a potentiostat and an electrochemical cell according to Fig. 5.



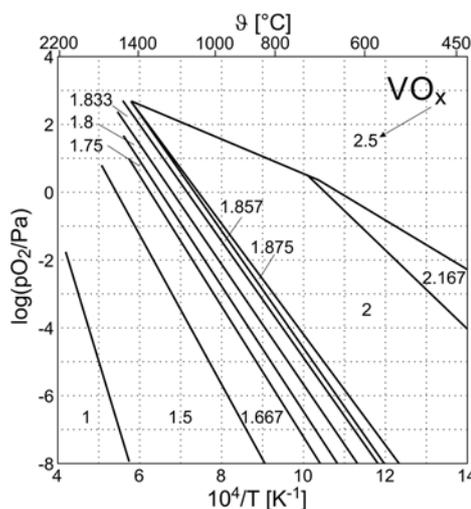
**Fig. 4.** Anodic polarisation curve of pure vanadium in 50 wt.-%  $\text{H}_2\text{SO}_4$  measured vs.  $\text{Ag}/\text{AgCl}$ ,  $\text{Cl}^-_{(\text{sat.})}$ .



**Fig. 5.** Electrochemical cell for the anodic oxidation and potentiometric measurements of partial selective electrodes; 1 partial selective electrode, 2 reference electrode, 3 Pt-counter electrode, 4 Haber-Luggin-capillary, 5 gas injection system, 6 gas outlet system.

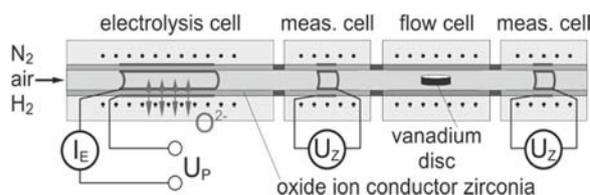
#### M 3

The gas phase oxidation method (CPO) offers the possibility to establish tailored oxidation states of vanadium oxides smaller than +5 by adjusting temperature and  $p_{\text{O}_2}$ . The thermodynamic ranges of the different oxidation states of vanadium given in Fig. 6 provide an orientation for the parameter adjustment in the gas phase.



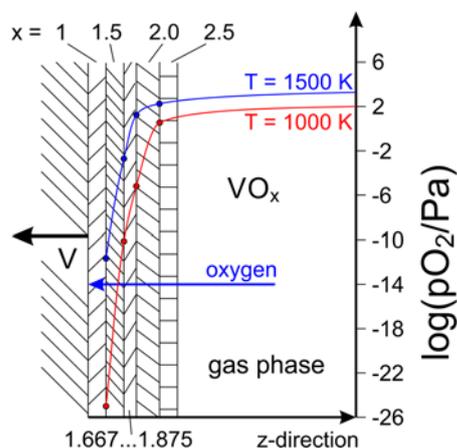
**Fig. 6.** Phase diagram of the system vanadium-oxygen published in [4].

As illustrated in Fig. 7, the oxygen partial pressure of a mixture of  $\text{N}_2/\text{air}/\text{H}_2$  is adjusted precisely within the range  $p(\text{O}_2) = 10^{-30} \dots 0.2\text{ bar}$  by a combination of a solid electrolyte pump cell and a solid electrolyte measuring cell [5]. After gas passage of the vanadium sample positioned in a separately heated transparent flow through cell, the oxygen partial pressure can be controlled again to measure the oxygen uptake by the vanadium surface [6]. Polished vanadium discs were placed inside the transparent cell and treated at different partial pressures and temperatures up to the point, where an oxide layer was visible by the unaided eye. Since the melting point of  $\text{V}_2\text{O}_5$  amounts to  $690\text{ }^\circ\text{C}$  in contrast to that of  $\text{VO}_2$  at  $1970\text{ }^\circ\text{C}$  the change between the two oxidation states could easily be noticed by the observer in the transparent cell at probe temperatures above  $690\text{ }^\circ\text{C}$ . This change from liquid  $\text{V}_2\text{O}_5$  to solid  $\text{VO}_2$  occurred at  $T = 1000\text{ K}$  at  $p_{\text{O}_2} \approx 100\text{ Pa}$  which is about on order of magnitude higher than indicated in Fig. 6.



**Fig. 7.** Schematic drawing of the experimental setup for gas phase oxidation of vanadium.

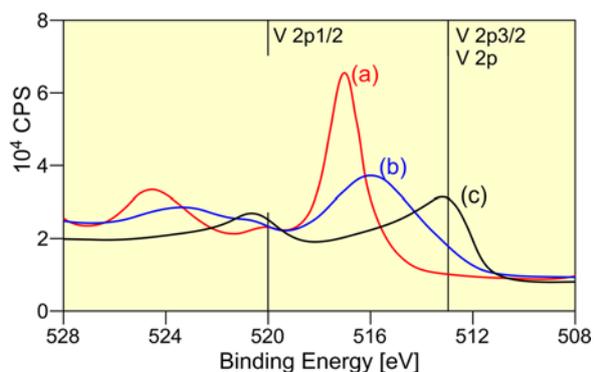
This  $pO_2$ -shift is caused by a kinetic phenomenon, the oxygen mass transfer from the gas phase to the oxide layer, enabling significant oxygen diffusion to the non-oxidized vanadium surface. This diffusion leads to a continuous increase of the thickness of the oxide layer and the corresponding oxygen consumption of the inner vanadium surface establishes a gradient of oxygen partial pressure within the oxide layer and the adjacent gas phase according to Fig. 8.



**Fig. 8.** Establishment of an oxygen pressure gradient at a heated vanadium surface due to oxygen diffusion through the oxide layers with different oxygen content  $x$ , calculation from thermodynamic data, published in [7].

Cooling the vanadium discs after heating to  $T = 1000$  K over 15 min at constant  $p(O_2)$  leads to different oxidation states, as results of XPS analysis of the prepared oxide layers given in Fig. 9 clearly indicate. Adjusting oxygen partial pressure at  $pO_2 \approx 1$  Pa the oxide surface is dominated by  $VO_2$  while  $pO_2 \approx 2 \cdot 10^4$  Pa leads to a surface consisting of  $V_2O_5$  exclusively.

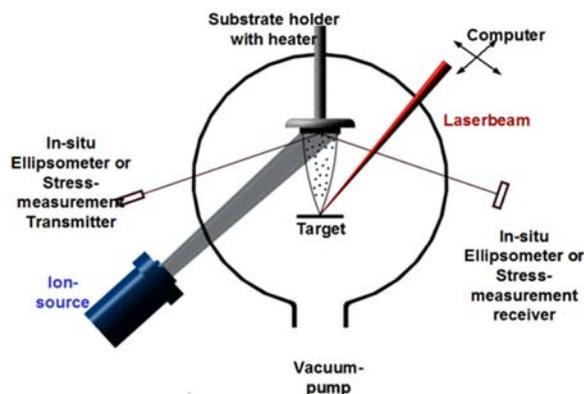
CPO with tailored temperature, oxygen partial pressure and treatment time enables therefore the separate adjustment of surface oxidation state and thickness of the oxide layer without introducing additional chemicals, essentially important for the electrode behaviour.



**Fig. 9.** XPS spectra of two different vanadium samples treated at  $700$  °C and (a):  $pO_2 = 2 \cdot 10^4$  Pa, (b):  $pO_2 = 4 \cdot 10^{-9}$  Pa compared to a spectrum of (c): polished metallic surface.

#### M 4

Vanadium oxide films with defined oxidation states were also prepared by using pulsed laser deposition (PLD) either in an oxygen background gas or with oxygen ion beam bombardment of growing films (see Fig. 10) [8].



**Fig. 10.** High vacuum pulsed laser deposition system used for the preparation of vanadium oxide films.

The method allows the preparation of metastable phases of vanadium oxide. For the preparation of the films, a KrF-excimer laser with 248 nm wavelength, 1 J laser pulse energy and 30 ns laser pulse duration was used for ablation from a pure vanadium target. For this, the laser beam was introduced into a high vacuum chamber and focused onto the target surface. A relatively high laser fluency of  $8$  J/cm<sup>2</sup> was used for ablation, the laser pulse repetition rate was 50 Hz. The films were prepared in an oxygen background gas using partial pressures in the range of  $p(O_2) = 5 \cdot 10^{-4} \dots 5 \cdot 10^{-2}$  mbar. The substrate temperature during film deposition was constantly  $400$  °C.

The method is characterised by a high degree of more than 50 % of ionised species having high mean kinetic energy of several 10 eV in the ablated particle current. The ablated vanadium particles collide on their way to the substrate with the oxygen molecules of the background gas resulting in the dissociation of the oxygen molecules. Thus, highly reactive oxygen atoms form and can combine with the vanadium atoms and ions at the substrate surface. In a proper energy range the metastable vanadium oxide VO phase is formed. This was established by measuring the ratio of oxygen and vanadium in the films by using EDX (see Table 2), which is nearly 1. The variation of the oxygen partial pressure did not lead to significant changes in this ratio, so metastable VO is formed at all applied background gas pressures.

## 2.2. Characterisation

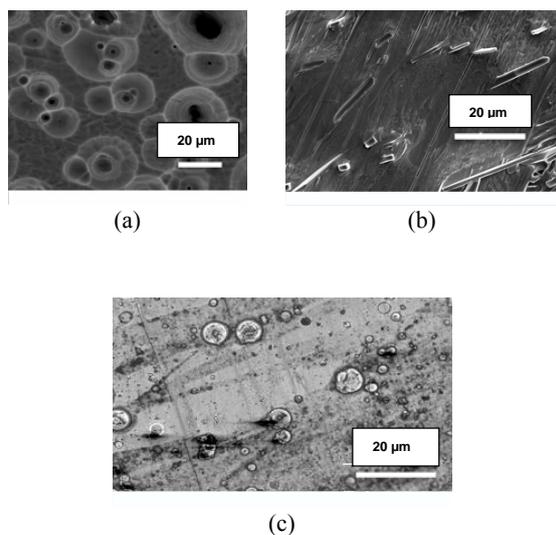
The preparation of vanadium oxides by method M 1 showed only irreproducible results. This was in accordance with [1], where investigations concerning

the passivation of Ti, Ta and W yielded in comparable observations. For that reason the following experiments have been executed with vanadium oxide-based electrodes prepared with the other oxidising methods.

**Table 2.** Composition of vanadium oxide films deposited by PLD at various oxygen partial pressures (Si results from the substrate and Pt from a thin conduction layer sputtered on the films. The thickness of the vanadium oxide films increased with increasing partial pressure so that the Si signal becomes smaller.)

p(O <sub>2</sub> ) [mbar]	O (W[%])	Si (W[%])	V (W[%])	Pt (W[%])
5.0E-04	22.93	47.2	26.45	3.5
5.0E-03	30.92	27.11	38.04	3.93
5.0E-02	41.63	13.63	43.03	1.71

Fig. 11 shows microscopic/ SEM shootings of the surfaces of the vanadium oxide based membranes generated on metallic structures demonstrating that the methods result in functional films that cover the whole surface but differ significantly in their microscopic appearance. It has to be stated that only M 3 and M 4 resulted in metal oxides with vanadium valences less than +5.

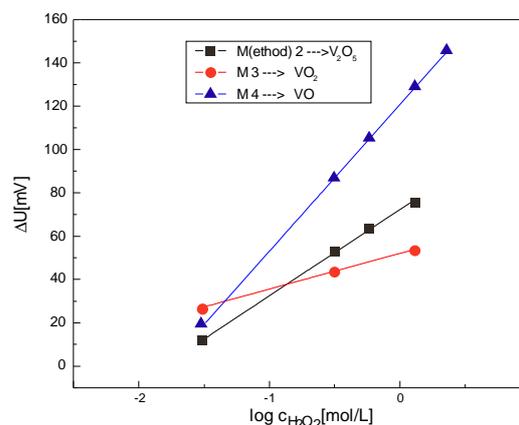


**Fig. 11.** SEM images of vanadium oxide films fabricated by different preparation methods; (a) V<sub>2</sub>O<sub>5</sub> formed by M 2 in 50 % H<sub>2</sub>SO<sub>4</sub> with a scan rate U<sub>P</sub>= 4.3 V vs. Ag/AgCl, Cl<sup>-</sup><sub>sat</sub> at  $\vartheta = 25$  °C; (b) VO<sub>2</sub> prepared by M 3; (c) VO formed by M 4.

Apart from the method-specific created different chemical compositions of the oxides determined by XPS measurements (an example was given in Fig. 9) these changes are mainly caused by variations of layer thicknesses. Furthermore, the layer presented in Fig. 11(c) contains a number of droplets, a known drawback of the PLD method.

## 2.3. Application

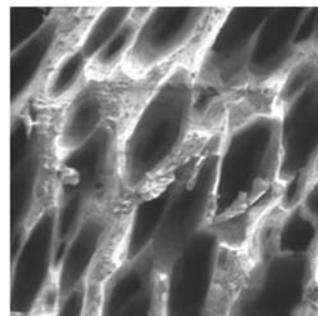
Fig. 12 shows that with all discussed methods sensory active systems of the type V/V<sub>x</sub>O<sub>y</sub> with partial sensitivity to H<sub>2</sub>O<sub>2</sub> are realisable. The investigated measuring range is fitted to the requirements of the galvanotechnical industry. The knowledge of H<sub>2</sub>O<sub>2</sub>-concentration is relevant for the correct adjustment of the ratio of Cu<sup>+</sup>/Cu<sup>2+</sup> in the electrolyte [9]. The electrode functions vary widely. While with M 2 there are method-conditioned restrictions in relation to the stoichiometry of the functional oxide, M 3 and M 4 offer clearly more options concerning the sensor optimisation. The highest sensitivity was obtained by the membrane produced with the PLD technology.



**Fig. 12.** Potentiometric determinations of H<sub>2</sub>O<sub>2</sub> with systems of the type V/V<sub>x</sub>O<sub>y</sub> realised by different preparation methods (M 2, M 3, M 4) at  $\vartheta = 25$  °C in 5% Na<sub>2</sub>SO<sub>4</sub> with additives of H<sub>2</sub>O<sub>2</sub> at pH ≈ 2 (all vs. Ag/AgCl, Cl<sup>-</sup><sub>sat</sub>); M 2: anodic oxidation, M 3: CPO; M 4: PLD.

## 3. Perspectives

Experiences gained from measurement campaigns with indicator electrodes for the determination of H<sub>2</sub>O<sub>2</sub> based on anodic oxidation of vanadium have demonstrated that a use of the pure transition group metal is unfavourable since the functional layers corrode quickly during the measurement (s. Fig. 13).



**Fig. 13.** Corroded electrode membrane after two week dwell time in a nickel electrolyte (ENTHONE) (mag. 500).

It has been proven to be advantageous to alloy vanadium with titanium before passivation playing an important role for the use of e.g. orthopaedic implants because of their corrosion stability and the improvement of the biocompatibility [10]. By adjusting an optimal alloy-ratio of both metals, it is possible to retain the functionality of the electrode over a very long period. In this context, results of corrosion measurements given in Fig. 14 clearly indicate that the corrosion stability of the electrode membrane can be increased significantly by adding titanium to the alloy.

For the choice of an appropriate alloy composition, it is necessary to investigate the upper alloying level of Ti at which the partial selectivity for hydrogen peroxide is maintained in appropriate degree. In the case

of the investigated V-Ti-alloys the optimal titanium content for the hydrogen peroxide determination with partially selective electrodes can be amounted to 20 wt.-% according to Fig. 14 and 15.

Investigations in [11] give rise to the assumption that the application of ternary alloys may lead to even better results. The method 4 offers in this field the best requirements. For instance by an introduction of different targets (V, Ti, Nb) in the PLD-chamber and a supply of an appropriate gas mixture for the oxidation the fabrication of ternary mixtures should be cheaper than a melting of the alloys with additional electrochemical oxidation [12].

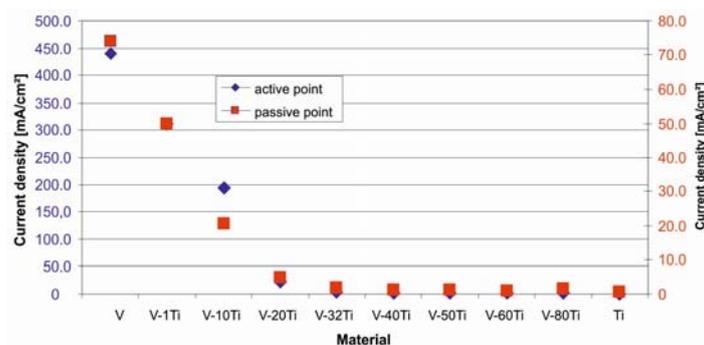


Fig. 14. Current density for activation  $j_a$  and passivation  $j_p$  of V-Ti-alloys.

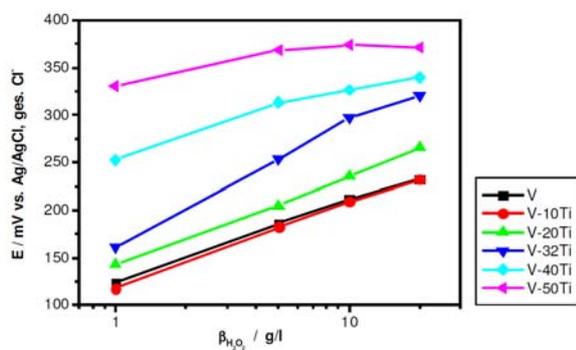


Fig. 15. Electrode functions of electrodes of V and V-Ti alloys vs. Ag/AgCl, Cl<sup>-</sup>sat in 5 wt.-% Na<sub>2</sub>SO<sub>4</sub> at  $\vartheta = 25^\circ\text{C}$  in a H<sub>2</sub>O<sub>2</sub> concentration range of  $b = 1 \text{ g/L} \dots 20 \text{ g/L}$ .

#### 4. Conclusions

Beside anodic passivation, also CPO and PLD deliver suitable vanadium oxide based membranes for the potentiometric determination of H<sub>2</sub>O<sub>2</sub>. The last two mentioned methods allow for vanadium in principle a largely variable realisation of oxidation states differing from the value +5. This has an impact on the performance of resulting electrochemical indicator electrodes. In future work, these effects shall be examined more closely and the new manufacturing methods for the specific application will be improved, too.

Because on pure vanadium based electrodes are not suitable for aggressive matrices the application of corrosion stable passivated binary or ternary vanadium alloys can be a reasonable alternative. This will require an optimisation process concerning the corrosion resistance and the necessary electrode sensitivity and selectivity. For the manufacturing process the PLD technology offers the best preconditions.

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