

New Methods for the Preparation of Partial Selective Redox Electrodes for the Determination of H₂O₂

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Abstract— In the paper, 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. The gas phase oxidation at controlled oxygen partial pressures (CPO) and the pulsed laser deposition (PLD) as an HV method are utilised as alternative methods beside the well established electrochemical passivation which leads usually 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.

Keywords—partial selective redox electrode; hydrogen peroxide, gas phase oxidation; pulsed laser deposition; electrochemical passivation

I. INTRODUCTION

Measurements of the oxidation/reduction potential (ORP) are suited for online determination of oxidising agents like halogens or hydrogen peroxide 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 the subgroups IV to VI of the periodic system are suited for this purpose [2]. The favourable sensory behaviour is related to the semiconducting and corrosion properties of the oxide layers with electronic and ionic defects.

The preparation of these layers was carried out so far by anodic oxidation [M(ethod 1)] in half concentrated acids (sulfuric and nitric acid) [3], leading usually to the highest possible valence state of the metal in use at the outer electrode surface. The inner oxide layer near the metal bulk can contain also lower valence states.

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

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 results of the determination of nitrite by means of a tungsten based indicator electrode at pH values between -1.4 ... 9 are given in Figure 2. There are two ranges with negligible influence

of the pH value (range 1: pH= -1.4 ... 1; range 2: pH= 4 ... 9) on the nitrite concentration related electrode potential. 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.

TABLE I. MEMBRANE MATERIALS FOR THE FABRICATION OF PARTIAL SELECTIVE ELECTRODES

analyte in aqueous phase	electrode material				
	Ti	Ta	W	Nb	V
Cl ₂	x	x	x		
Br ₂	x	x	x	x	
I ₂			x		
NO ₂ ⁻			x		
H ₂ O ₂					x
Fe ³⁺	x				

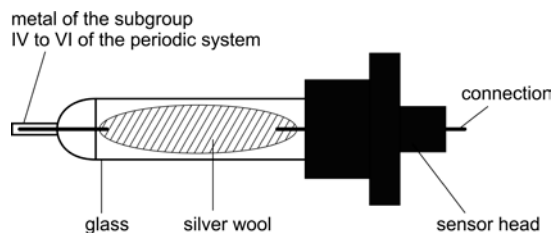


Figure 1. Redox electrode with passivated metal rod as partial selective membrane

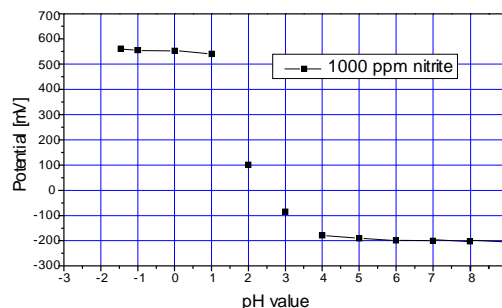


Figure 2. Nitrite determination with tungsten oxide electrodes

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 possess several lower oxidation states with sufficient chemical stability.

In section II, the preparation of the redox electrode by PLD and CPO is described. SEM pictures of the generated vanadium oxide layers and the results of the potentiometric determination of H_2O_2 are presented in section III.

II. NEW METHODS

For the determination of H_2O_2 with partially selective redox electrodes of the above mentioned type vanadium based electrodes are used [4]. Figure 3 shows an electrochemical polarisation curve in sulfuric acid obtained with a vanadium electrode (purity > 99.8 %) within the range of $U_p = 0 \dots 6$ V vs. Ag/AgCl, $Cl^-_{(sat.)}$ at the scan rate 100 mV/s. The observed colour changes of the vanadium surface seem to be related with the formation of VO (green), VO_2 (blue-black) and V_2O_5 (orange) as the final state.

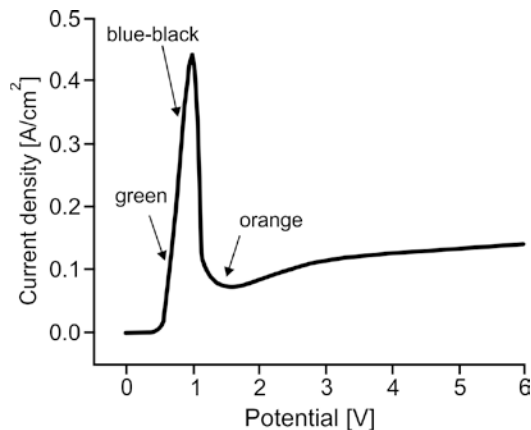


Figure 3. Anodic polarisation curve of pure vanadium in 50% H_2SO_4 measured vs. Ag/AgCl, $Cl^-_{(sat.)}$

A further possibility for the preparation of vanadium oxide layers with tailored valence state is the gas phase oxidation at controlled temperature and oxygen partial pressure [CPO (M2)] according to Figure 4 [5].

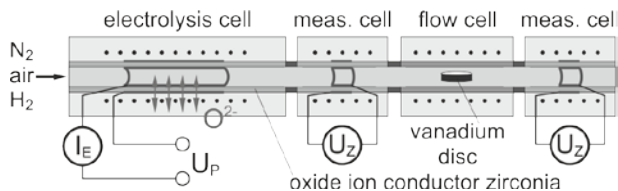


Figure 4. Schematic drawing of the experimental setup for gas phase oxidation of vanadium

The oxygen partial pressure of a mixture of $N_2/air/H_2$ is adjusted precisely within the range $p(O_2) = 10^{-30} \dots 0.2$ bar by a combination of a solid electrolyte pump cell and a solid

electrolyte measuring cell [6]. 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 [7]. 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.

Vanadium oxide films with defined oxidation states were realised also by using pulsed laser deposition (PLD) either in oxygen background gas or with oxygen ion beam bombardment of growing films (M3) [8] (see Figure 5).

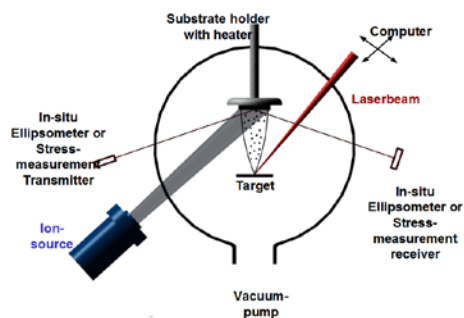


Figure 5. High-vacuum pulsed laser deposition system used for the preparation of vanadium oxide films

The method was used because it allows the preparation of metastable phases of vanadium oxide.

III. EXPERIMENTAL RESULTS, DISCUSSION, OUTLOOK

Figure 6 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.

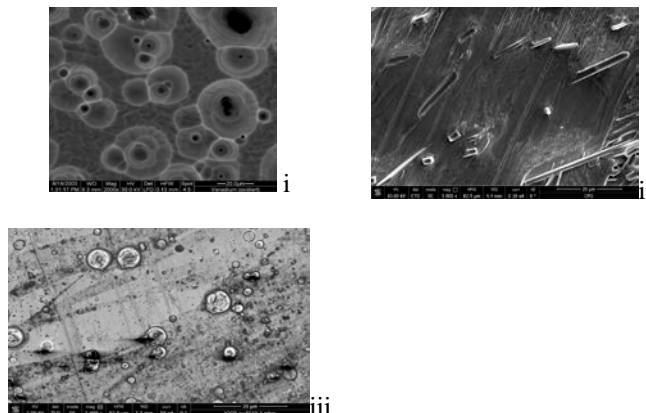


Figure 6: SEM images of vanadium oxide films fabricated by different preparation methods; i: V_2O_5 formed by M1 in 50% H_2SO_4 with a scan rate $U_p = 4,3$ V vs. Ag/AgCl, Cl^-_{sat} at $\theta = 25$ °C; ii: VO_2 prepared by M2 iii: VO formed by M3

Apart from the method-specific created different chemical compositions of the oxides this fact mainly is caused by varying layer thicknesses. Furthermore, the layer presented in Figure 6iii contains a number of droplets, a known disadvantage of the PLD method.

Figure 7 shows that with all mentioned methods sensory active systems of the type V/V_xO_y with partial sensitivity to H_2O_2 are realisable. The electrode functions vary widely. While with M1 there are method-conditioned restrictions in relation to the stoichiometry of the functional oxide, M2+M3 deliver clearly more options concerning the sensor optimisation.

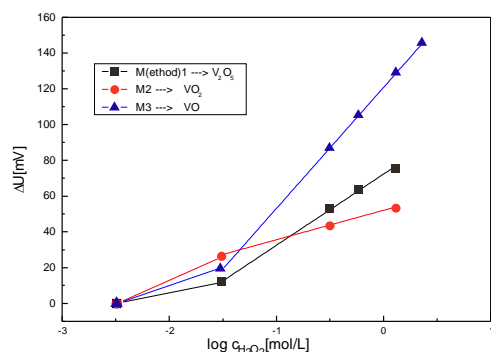


Figure 7. Potentiometric determinations of H_2O_2 with systems of the type V/V_xO_y vs. $Ag/AgCl, Cl^-_{(sat.)}$ realised by different preparation methods (M1, M2, M3) at $\vartheta = 25^\circ C$ in 5% Na_2SO_4 with additives of H_2O_2 at $pH \approx 2$; M1: anodic oxidation, M2: CPO; M3: PLD

Experiences gained from previous work on indicator electrodes for the determination of H_2O_2 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.

It has proved an advantage to alloy vanadium with titanium before passivation [9]. 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 Figure 8 clearly indicate that the corrosion stability of the electrode membrane can be increased significantly by adding titanium to the alloy.

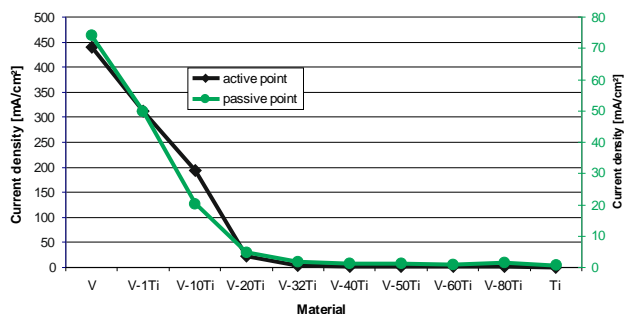


Figure 8. Current density for activation j_a and passivation j_p of V-Ti-alloys

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 at the required level.

Further studies within the scope of the work in process presented here include the following activities:

- creation and evaluation of oxidised alloy coatings based on M2+M3
- examination of the thesis supported in [10] that in the use of vanadium-titanium alloys as membrane material there is no need for an oxidation of the metals and realisation of such alloys by means of M2+M3

IV. CONCLUSIONS

Beside anodic passivation, also CPO and PLD deliver suitable vanadium oxide based membranes for the potentiometric determination of H_2O_2 . The last two mentioned methods allow in principle a largely variable realisation of oxidation states for the vanadium 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 are to be improved, too.

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