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Voltammetry on BIMEVOX.10 (ME = Cu, Ni, Zn, Mg) microsamples

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Abstract

High temperature cyclic voltammetry on microsamples was used for the investigation of the electrochemical stability of BIMEVOX.10 materials. The electrochemical measurements were performed on a three-electrode cell of the type: Pt[microsample|YSZ|Pt with the interface Pt|YSZ as a pseudo reference electrode. The experiments were performed in nitrogen containing a small quantity of oxygen. The cell consisted of a disc of yttria stabilized zirconia (YSZ) with platinum paste electrodes for the counter and the reference electrode. The working electrode was a small platinum plate which contacts the microsample and presses it onto the surface of the YSZ disc. In general, the stability of BIMEVOX.10 is determined by the stability of the main compound Bi_2O_3 . None of the samples exhibited a substantially higher stability against complete reduction than BICUVOX.10. Nevertheless slight differences in the reduction processes at less negative potentials than the standard potential of Bi_2O_3 have been observed. Redox processes in this potential region could be related to valence changes of vanadium from V^{5+} to V^{4+} and, at more negative potentials, from V^{4+} to V^{3+} . © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Members of the BIMEVOX family ($\text{Bi}_4\text{V}_{2(1-x)}\text{Me}_{2x}\text{O}_{11-3x}$) of oxygen ion conductors exhibit a larger electrical conductivity at temperatures below 500°C [1] than other oxygen ion conductors like yttria stabilized zirconia (YSZ). This makes them potentially interesting for applications in fuel cells, sensors or oxygen separation membranes. The main disadvantage for Bi_2O_3 based materials is the poor stability against reducing conditions. Previous

investigations on $\text{Bi}_2\text{O}_3\text{-Y}_2\text{O}_3$ by Takahashi [2] and on $\text{Bi}_2\text{O}_3\text{-Er}_2\text{O}_3$ by Verkerk et al. [3] revealed the electrochemical stability limit to be close to that for Bi_2O_3 calculated from the free enthalpy of formation ΔG_f^0 . This corresponds to an oxygen partial pressure of $p_{\text{O}_2} = 10^{-13.1}$ atm at 600°C. In contrast to these results a decomposition limit of $p_{\text{O}_2} = 10^{-20}$ atm was found by Jurado et al. [4] for the same materials. For BICUVOX and BINIVOX a limit of $p_{\text{O}_2} = 10^{-6.7} - 10^{-10}$ atm was given by Iharada et al. [5]. The exact knowledge of the operating range is necessary for decisions about future applications. The operating range is not only determined by the stability of the material but also by the changes of the electrical

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properties, i.e. the transference number, related to changes of oxygen stoichiometry from partial reduction of the electrolyte.

A characterization of the electrochemical properties of BIMEVOX was carried out by Iharada et al. [5] involving the determination of redox stability interval by a potential relaxation technique, measurement of ionic transference number by determination of current efficiency in an oxygen pump, electrode polarization by impedance measurements at different oxygen partial pressures, and potentiometric measurements. These results suggested the above mentioned stability range and n-type electronic conductivity of a few percent increasing with lower oxygen partial pressure. Voltammetric studies on the interface Pt|BICUVOX.10 by Breiter et al. [6] showed a much lower electrode polarization resistance R_p compared with that on Pt|YSZ. From the temperature dependence of R_p it was concluded that the same rate determining step is valid for the oxygen reduction in both systems. The lower R_p values were explained by an increase of the active surface area on BICUVOX itself introduced by a small electronic conductivity. A similar conclusion about extension of the active surface area was made by Vinke et al. [7] for erbia stabilized bismuth oxide where p-type electronic conductivity was predicted [8].

Boivin et al. [9] investigated reduction processes by X-ray diffraction in different BIMEVOX and the parent compound $\text{Bi}_4\text{V}_2\text{O}_{11}$ in a hydrogen atmosphere. They found that $\text{Bi}_4\text{V}_2\text{O}_{11}$, not reduced beyond the composition $\text{Bi}_4\text{V}_2\text{O}_{10.66} = \text{Bi}_2(\text{V}_{1-x}^{\text{V}}\text{V}_x^{\text{IV}})\text{O}_{5.5-x/2}$ with $x=0.33$, can be re-oxidized to the original structure. A stronger reduction leads to a destruction of the electrolyte. Similar processes were proposed for BIMEVOX. These materials were used in an oxygen pump. From the current–voltage relation an enlargement of the active surface area was also predicted. The origin of electronic conductivity was related to the reduction of part of V^{5+} to V^{4+} .

Voltammetric measurements on BICUVOX.10 microsamples [10] confirmed the results of Takahashi [2] and Verkerk et al. [3] for the decomposition limit of Bi_2O_3 -based materials. In addition this technique allows the determination of other redox processes in the sample within the stability

range responsible for the formation of electronic defects. In the present paper a comparison of the measurements on different BIMEVOX.10 compounds will be given.

2. Experimental

Electrochemical measurements were made in a fully automated system in the temperature range 450–700°C. The cell was placed in a holder covered by a glass tube which can be flushed by different gases. A detailed description of the experimental set-up can be found in Ref. [11]. The measurements were performed on a three-electrode cell of the type: Pt|microsample|YSZ|Pt with the interface Pt|YSZ as a pseudo reference electrode. The cell, shown in Fig. 1, consisted of a disc of YSZ with platinum paste electrodes for the counter (CE) and the reference electrode (RE). The YSZ serves as a kind of inert and electron blocking supporting electrolyte.

The nominal composition of the BIMEVOX.10 material was $(\text{Bi}_4\text{V}_{2(1-x)}\text{Me}_{2x}\text{O}_{11-3x})$ where $x=0.1$ for all dopants. Single crystals or ceramics from the same batch were already characterized by DTA, impedance spectroscopy, X-ray diffraction [12,13] and for $\text{Me}=\text{Cu},\text{Ni}$ by electron diffraction [14,15].

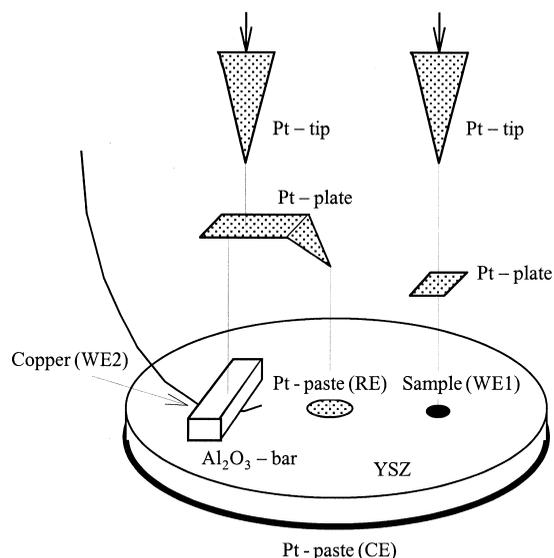


Fig. 1. Schematic diagram of the electrochemical cell for voltammetric measurements at high temperatures.

Very small pieces of the BIMEVOX.10 were cut from these single crystals. The size of the samples varied from piece to piece. It was not determined for every sample because of difficulties in handling such small pieces. From optical measurements of the volume of molten BICUVOX.10 microsamples we know that the mass of such samples is in the range of a few micrograms [10].

The samples were pressed onto the surface of the YSZ disc by a small platinum plate which acts as the working electrode (WE) and provides contact. All experiments were performed in nitrogen. Some residual oxygen in the gas is necessary to protect the sample against chemical reduction and for a stable potential of the RE. It is in the range of -0.2 V to -0.3 V versus the reversible oxygen electrode at 1 atm O_2 (ROE) for all experiments. This corresponds to an oxygen partial pressure of approximately $p_{O_2} = 10^{-6}$ atm. It should not be too high to avoid an overlapping current from the reduction of oxygen at the WE.

Because of the unknown (but stable) oxygen partial pressure in the chamber the potential of the RE has to be determined in relation to a defined reference system. For a better comparison of the data, all potentials are given versus the reversible oxygen electrode at 1 atm O_2 (ROE). The potential scales of all voltammograms also refer to ROE. We did the necessary calibration by a voltammetric measurement on copper wire which allowed an accurate determination of the potential of the RE. In these measurements the two equilibrium potentials $E_{vs.RE}^{Cu/Cu_2O}$ and $E_{vs.RE}^{Cu_2O/CuO}$ of the two reduction/oxidation processes were determined versus the potential of the RE. From thermodynamic data in the literature [16] the equilibrium potentials versus ROE can be calculated ($E_{vs.ROE}^{Cu/Cu_2O}$ and $E_{vs.ROE}^{Cu_2O/CuO}$). Therefore the new potential scale versus ROE ($E_{vs.ROE}^{Sample}$) is given by Eq. (1) or (2).

$$E_{vs.ROE}^{Sample} = E_{vs.RE}^{Sample} - E_{vs.RE}^{Cu/Cu_2O} + E_{vs.ROE}^{Cu/Cu_2O} \quad (1)$$

$$E_{vs.ROE}^{Sample} = E_{vs.RE}^{Sample} - E_{vs.RE}^{Cu_2O/CuO} + E_{vs.ROE}^{Cu_2O/CuO} \quad (2)$$

A voltammogram on copper was taken just before and after the measurements on the sample without changing the temperature or gas flow to check the stability of the RE potential.

Experiments were carried out between 450°C and 750°C in 50°C steps. For every temperature a fresh sample has to be used because of the irreversible decomposition of the ternary oxide during the first cathodic scan. The first potential sweep applied to the WE goes into the anodic direction from 0 to $+0.3$ V relative to the potential of the RE. Then a cathodic scan to -1 V was applied, followed by an anodic scan back to 0 V. Three complete cycles were taken at a scan rate of 1 mV/s for the BIMEVOX.10 microsamples and at a scan rate of 10 mV/s for the copper electrode. The slow scan rate for BIMEVOX.10 is necessary to enhance the sharpness of the peaks and to allow complete reduction or oxidation of the microsample during one cycle. The determination of the different onset potentials of the peaks had to be carried out at a sufficiently large current scale to achieve a satisfactory accuracy.

3. Results and discussion

3.1. Precision and stability of the reference potential

The check of the reference electrode before and after a measurement revealed a very good stability of the reference potential. Although our RE does not operate as a reversible oxygen electrode at temperatures as low as 450°C , its potential did not shift by more than 5 mV during the time of an experiment which took about 4 h. At lower temperatures the determination of the equilibrium potential of the two redox reactions on copper became problematic because of broadening of the peaks, caused by the formation of a passive oxide layer, and the decrease of reversibility which leads to an uncertainty of approximately 100 mV at 450°C . Alternatively measurements on copper oxide microsamples allow a much more precise determination of the equilibrium potentials [17]. However, they fail to a large extent because of problems contacting a very small amount of powder. It was not used as a reference system therefore. The calibration with values from voltammograms on copper oxide microsamples, obtained in separate experiments for the whole temperature range, comparison with those on copper wire, and comparison of the potential difference between the

two equilibrium potentials with theoretical values yielded a precision of about 10 mV.

3.2. Voltammograms of BIMEVOX.10 microsamples

The new results on BICUVOX.10 microsamples obtained from single crystals, pressed onto YSZ, were similar to those for molten microsamples from polycrystalline material [10]. Fig. 2 displays a voltammogram with enlarged current scale for BICUVOX.10. In Fig. 3 the same measurement is shown with regular scale. A voltammogram of the empty cell with the interface Pt|YSZ, measured at the same temperature using the same platinum plate as WE, is shown as a baseline. The oxygen partial pressure was slightly higher for the measurement of the empty cell as indicated by a slightly larger cathodic current at the negative potential of reversal and a 6 mV more positive potential of the RE. Similar responses were found for all BIMEVOX.10. Figs. 4 and 5 display a measurement on BIZNVOX.10 as an example.

Current peaks of oxidation–reduction processes around 0 mV vs. ROE at 650°C were identified to be adsorption/desorption of an oxygen layer on platinum [18] by comparison with the baseline. Electrochemical redox processes in BIMEVOX.10 microsamples occurring within this potential region

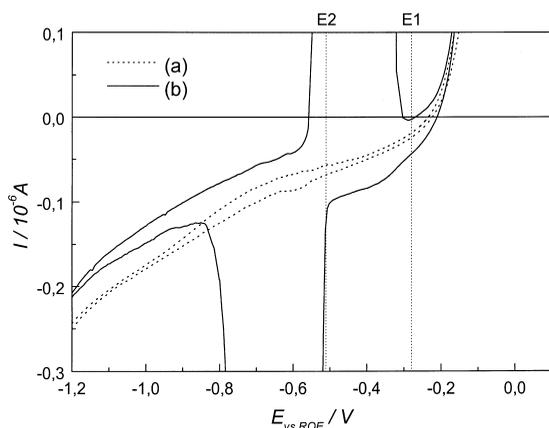


Fig. 2. Voltammogram of the empty cell (a) compared to that of the first cycle on BICUVOX.10 (b) displayed with enlarged current scale. Measurement in nitrogen at 650°C, at a scan rate of 1 mV/s. Vertical dotted lines designate the measured potentials.

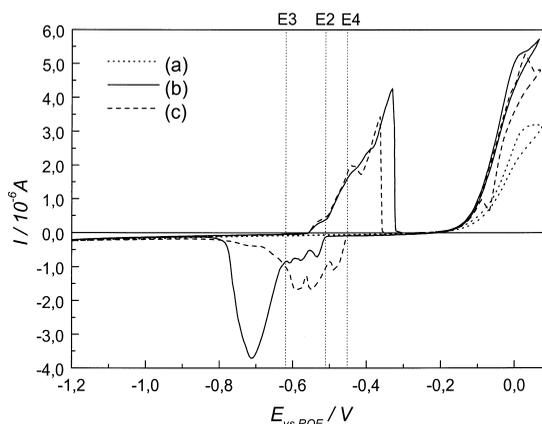


Fig. 3. Voltammogram of the empty cell (a) compared to that of the first (b) and second cycle (c) on BICUVOX.10 in regular scale.

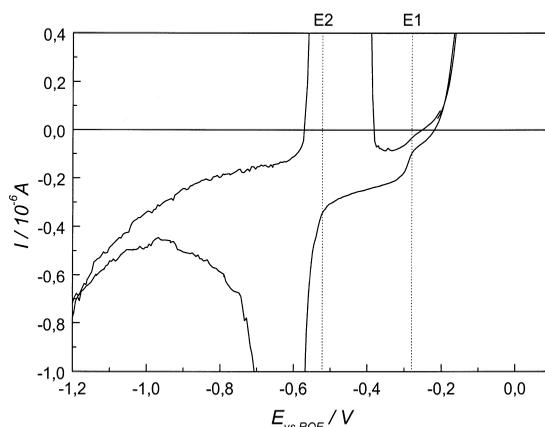


Fig. 4. Voltammogram of the first cycle on BIZNVOX.10 displayed with enlarged current scale. Experimental conditions and symbols see Fig. 2.

will be obscured by relatively large currents from the formation of the oxygen layer on platinum and oxygen evolution. It must be said that BIMEVOX.10 may already be in a partly reduced state at zero polarization in the inert gas. Several intermediate oxides between V_2O_5 and V_2O_4 exist for vanadium. The equilibrium potentials of the corresponding transitions are positive against the actual potential of the RE. On the other hand, equilibrium potentials of the redox processes in pure oxides and redox processes in the BIMEVOX.10 compounds cannot be

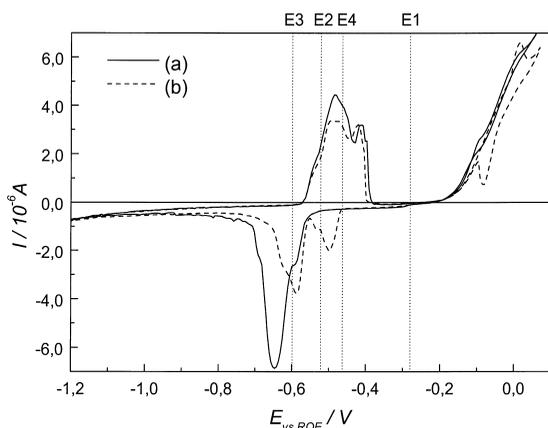


Fig. 5. Voltammogram of the first (a) and second cycle (b) on BIZNVOX.10. Experimental conditions and symbols see Fig. 2.

compared directly. Therefore conclusions about this domain cannot be made.

A comparison of the cathodic scan in Fig. 2 on BICUVOX.10 with that of the baseline between -200 and -500 mV displays for BICUVOX.10 a slightly larger current, although the contact area and oxygen concentration in the gas are approximately the same ones. At about -300 mV a weak wave is visible. Cathodic currents in this potential region could have three reasons: (a) reduction of oxygen coming from the ambient gas, (b) partial change of the oxidation state of vanadium, or a combination of (a) and (b). Some facts indicate that this reduction current is indeed a combination of (a) and (b). The onset potential E1 of the weak wave in Figs. 2 and 4 coincides very well with the calculated equilibrium potential of the V_2O_5/V_2O_4 transition in pure vanadium oxides. At more positive potentials stable phases exist in pure vanadium oxides with formal fractional valence states of vanadium like $V^{4.667+}$ and $V^{4.333+}$. The formation of V^{4+} defects introduces electronic conductivity at the surface of BIMEVOX which extends the active electrode region. Part of the vanadium at the surface is immediately re-oxidized by the ambient oxygen. The total flux of oxygen from the gas phase and therefore the re-oxidation rate will increase with the active surface area. For any applied potential the rate of electrochemical reduction which is proportional to the measured current and the rate of chemical oxidation

must be equal. This situation can be achieved by the variation of the active surface area and holds for the assumption of stationary conditions, practically fulfilled for our low scan rate at least at higher temperatures. Similar processes like electrochemical reduction of the electrolyte and increase of the active surface area have been observed in voltammetric measurements on large BICUVOX.10 samples [6].

Between -500 mV and -600 mV up to three peaks are visible which were more pronounced on smaller samples (compare Figs. 3, 5 and 6). This might be related to the progression of the reduction process from V^{4+} to V^{3+} through several intermediate stages. In pure vanadium oxides intermediate phases, the so called Magnéli-phases, exist between the oxidation states V^{4+} and V^{3+} . Magnéli-phases are a series of homologous compounds of the general formula V_nO_{2n-1} with $n > 2$. Again it must be said that a direct comparison of the equilibrium potentials for these transitions in pure vanadium oxides and in the BIMEVOX compounds is not feasible. Only magnesia stabilized material seems to have a higher stability against the V^{4+}/V^{3+} transition because no peaks were observed in this potential region during the first cathodic scan (Fig. 7). Moreover, we did not observe the weak wave at less cathodic polarization.

The coincidence of the onset potential of the main peak with the calculated equilibrium potential of the Bi_2O_3/Bi transition has already been discussed in

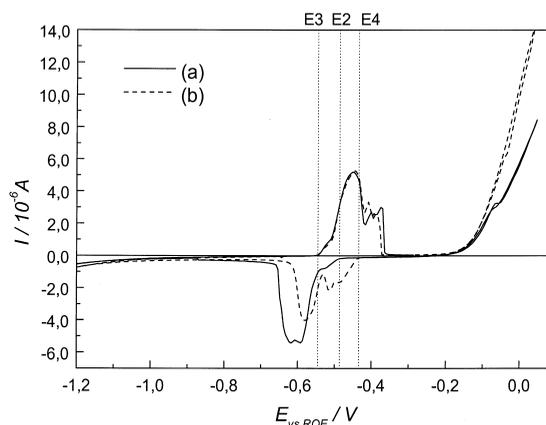


Fig. 6. Voltammogram of BINIVOX.10 at 700°C . (a) First cycle, (b) second cycle.

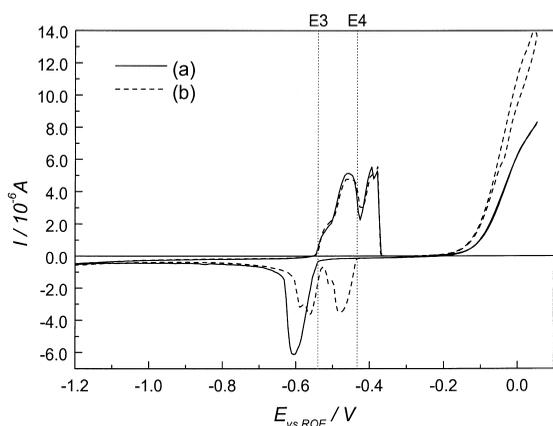


Fig. 7. Voltammogram of BIMGVOX.10 at 700°C. (a) First cycle, (b) second cycle.

previous papers [10,17] for BICUVOX.10. Polarization beyond the main peak is accompanied by the full disintegration of the BIMEVOX structure. Scanning electron microscopy of the residues on the Pt-platelets which were used for contacting the sample revealed the presence of Bi-rich and V-rich phases separated from each other. The substances were ordered in concentric rings with vanadium in the center and bismuth in the outer area. This can be explained by the low melting point of bismuth (271°C) under the assumption that the oxide was reduced to the metal state.

The second and the third scan have a more or less equal shape. Since there are separate V- and Bi-rich phases after the reduction we found peaks for the

oxidation/reduction of vanadium oxides between 0 V and -0.2 V (see Figs. 3, 5, 6 and 7). The measured equilibrium potential of this redox reaction does not agree with the calculated one for the V_2O_5/V_2O_4 electrode. It is close to that of the V_2O_5/V_3O_7 electrode. In Ref. [17], where pure vanadium oxides were measured, the reduction of V_2O_5 to V_2O_4 was identified as the first step.

Two or more large peaks were observed at more negative polarization. The first reduction peak in the second and third scan coincides with the *measured* equilibrium potential on pure bismuth-oxide microsamples as already noticed in Ref. [17]. It is not clear why the measured and the calculated equilibrium potentials for Bi_2O_3 differ by more than 100 mV from each other. One explanation could be the electrochemical formation of meta-stable BiO which normally decomposes above 180°C. Another explanation is the direct conversion of V_2O_5 to V_2O_3 for which the calculated equilibrium potential is close to E4 (see Fig. 8). However this is not very probable since the shape of the reduction and its corresponding oxidation peak looks very similar to that observed in measurements on pure Bi_2O_3 [17].

Table 1 contains data concerning the temperature dependencies of the onset potentials E1 of the first weak wave after current reversal in the first cathodic scan, E2 of the second weak peak in the first scan, E3 of the main reduction peak in the first scan and E4 of the first reduction peak in the second and third scan. The potentials do not change very much with the type of dopant. Differences between these values

Table 1

Measured values for E1, E2, E3, E4 versus ROE^a

Temp. K	BICUVOX.10				BINIVOX.10				BIMGVOX.10				BIZNVOX.10			
	E1 mV	E2 mV	E3 mV	E4 mV												
723	-362	-540	-754	-551	*	*	-764	-595					*	*	-709	-546
773	*	-557	-696	-530	-344	-577	-712	-522					-306	*	*	-522
823	-311	*	-674	-506	*	-540	-683	-514					-297	-564	-661	-490
873	-282	-527	-619	-468	-299	-507	-648	-490					-291	-544	-641	-477
923	-279	-511	-619	-452	-268	*	-574	-459	*	*	-599	-449	-274	-513	-589	-457
973	*	*	-559	-479	-247	-492	-558	-470	*	*	-557	-438	-272	-487	-539	-434
1023													-274	-459	-504	-411

^a All values are averages of several measurements. Measurements were not available for the open spots. A determination of the respective values was not possible for spots marked with a star.

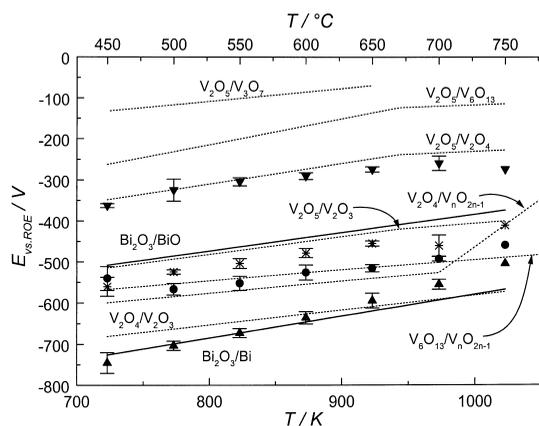


Fig. 8. Comparison of the measured potentials with calculated values of some reactions. For the equilibrium potential of V_6O_{13}/V_nO_{2n-1} only one line of a series of lines close together is given for clarity. The same was done for V_2O_4/V_nO_{2n-1} . The mean values over all compounds are represented by symbols: rectangles, E1; circles, E2; triangles, E3; and stars, E4. Error bars show the standard deviation.

are considered to be caused by random errors. In Fig. 8 average values of all compounds for E1–E4 are displayed with error bars therefore.

4. Conclusion

Cathodic currents at moderate negative polarization were related to a partial electrochemical reduction of part of the vanadium in equilibrium with the chemical re-oxidation by oxygen from the ambient atmosphere. Differences in the redox processes between -0.2 V and -0.55 V were observed in the voltammograms between BIMGVOX.10 and the other compositions maybe because of a better stability of BIMGVOX.10 against the reduction of V^{4+} to V^{3+} . The stability against complete reduction which is related to the reduction of Bi_2O_3 to bismuth metal and accompanied by the destruction of the material is the same for all materials under study.

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