Voltammetric measurements on Me_xO_y (Me = Bi, Cu, V) compounds and comparison with results for BICUVOX.10

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Abstract

Voltammetric measurements on cells of arrangement Pt,Ar|sample|YSZ|Ar,Pt with a very small sample mass ('microsamples') turned out to be a very convenient tool for the determination of thermodynamic properties of oxides. Measurements were made on Bi_2O_3, CuO and V_2O_5 microsamples and on nickel and copper metal between 550 and 700°C. The measurements on nickel were used for the calibration of the reference electrode. The measurements on CuO showed the advantage of the use of microsamples. Comparison of the results for CuO with the standard potential, calculated from thermodynamic data in the literature, revealed the high accuracy of the method. In the case of measurements on V_2O_5 a possible reaction path was identified. The vanadium system is very complicated because of the large number of stable oxidation states for vanadium in V_xO_y compounds. The measurements on Bi_2O_3 showed a large deviation of about 100–150 mV from the calculated equilibrium potentials. BICUVOX.10 microsamples are reduced irreversibly below -570 mV against a reversible oxygen electrode in 1 atm O_2 at 600°C in the first negative sweep. The voltammograms for BICUVOX.10 are compared with measurements on pure Me_xO_y compounds and with calculated data. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Yttrium stabilised zircondioxide (YSZ) has excellent stability against reduction, a low electronic conductivity over a wide range of oxygen partial pressures or potential range and acceptable oxygen ionic conductivity with a transference number of one for oxygen ions at temperatures above 500°C. It is therefore suitable and widely used as a sensor material for the measurement of the oxygen partial pressure in gases by potentiometric and amperomet-

ric methods. The high thermal and mechanical stability of YSZ allows the examination of oxygen activity in melts by direct immersing of tubes. YSZ has also been used as an electrolyte in cells for the determination of the oxygen activity in solids and for the measurement of the Gibb's energy of formation of oxides by potentiometric methods. Voltammetric measurements on such cells were made for the investigation of the thermodynamic properties of different metal oxides and their properties as electrode material. High temperature voltammetry has become an important technique in solid state electrochemistry. It is supplementary to impedance techniques for the study of the electrode|solid electrolyte

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interface. For instance, it was applied to the characterisation of the interface between a metal electrode and a YSZ surface modified by iron implantation for the enhancement of the performance of the oxygen electrode [1]. Oxidation and reduction processes of the implanted iron under a sputtered gold electrode were observed in agreement with the thermodynamic potentials of iron oxides. It was concluded that the diffusion of electrons or holes to the fixed iron ions is the rate determining process.

Voltammetry was also used for the observation of oxidation–reduction phenomena in metal/metal oxide systems [2]. There the samples were in the shape of a large pellet and the reference electrode was a Ni/NiO mixture of the same shape.

The problems of large electrodes with semi-infinite extension are: (a) broadening and shift of the observed oxidation and reduction peaks due to non-ideal conditions according to the voltammetric theory for diffusion limited redox processes; (b) a shift of the peak potentials because of the iR-drop at high currents.

By the introduction of 'microsamples' the above difficulties can be reduced. This technique was used recently for the study of redox processes in BICUVOX.10 [3]. BICUVOX is the designation of a family of oxygen ion conductors based on Bi_2O_3 [4]. Additional work was performed on pure oxides in order to demonstrate the reliability of the method and for a comparison with the results for BICUVOX.10.

2. Experimental

The measurements were carried out in the temperature range between 550 and 700°C in a fully automated setup based on the Solartron ECI 1286. A detailed description of the setup is given in Ref. [5]. The whole cell was kept in a special holder in a quartz glass tube which can be flushed with different gases. The cell consisted of a disk of YSZ from Friatec containing 8 mol% Y_2O_3. It had a diameter of 0.5 cm and a thickness of about 0.03 cm. The surface was polished up to 8 μm and cleaned in an ultrasonic bath. The counter electrode (CE) was produced by unfluxed platinum paste which entirely covered one side of the disc. On the opposite side of the disk the sample was attached in different ways

(molten or pressed) depending on the type of sample, and contacted with a small sheet of platinum. The reference electrode (RE) was a small point of platinum paste on the same side of the YSZ disc contacted with a platinum tip (Fig. 1). The whole cell was flushed with argon at a purity of 99.999% during an experiment.

For determination of thermodynamic data knowledge of the potential in relation to a defined reference potential, commonly the potential of the reversible oxygen electrode at 1 atm O_2 (ROE), is important. This relation was determined by an independent voltammetric measurement on the Ni/NiO system. For this a pure nickel wire was used as a second working electrode and pressed on the YSZ. A voltammogram of the nickel wire was measured just before and after measurement on the sample without change of temperature or configuration. The potential of the RE and its stability over time was determined from its relation to the reversible potential of the Ni/NiO electrode. A detailed description of the procedure and the reliability of the result of the calibration is given in Ref. [3].

A high temperature pre-treatment of the cell was performed to eliminate errors from organic contamination of the sample and the electrodes. The cell was heated to 600°C and kept for about 1 h in 100% O_2. In addition, three cycles from 0 to $+ 0.3$ V and back
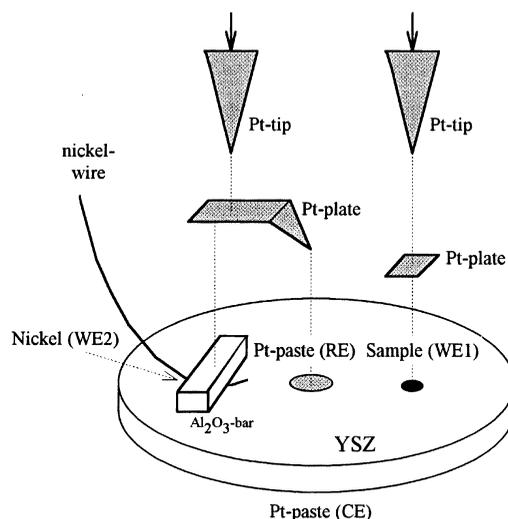

Fig. 1. Schematic diagram of the electrochemical cell for voltammetric measurements at high temperatures.

to 0 at 50 mV/s were applied to the WE. After this procedure the gas was switched to argon, a constant temperature between 550 and 700°C was established in 50°C steps and a measurement was performed. The first scan extended from 0 against the RE to + 0.3 V. Then a negative scan to − 1.0 V was applied, followed by a positive scan back to 0. Three complete cycles were made in all measurements at a scan rate of 1 mV/s. The slow scan rate is necessary to enhance the sharpness of the peaks and to allow complete reduction or oxidation of the microsample during one cycle. Generally, two different types of sample were used, either as powder or as a small piece molten onto the YSZ. In both cases the contact was made by a sheet of platinum.

Samples with a purity of 99.99% or better were used in all cases. CuO was applied as a powder to the YSZ surface. The mass of the sample could not be determined because weighing was not sufficiently sensitive. An estimation of the weight by measuring the volume of the sample with an optical microscope, as in Ref. [3] for BICUVOX.10, was not done because of the relatively high melting point of CuO. Measurements were also made on a small flake of Cu metal. This piece was simply pressed onto the YSZ and contacted with a platinum tip. Bi_2O_3 was applied in both ways, by melting and as powder. The mass of the molten sample, which could be determined via the volume, was in the range of a few micrograms. In the case of V_2O_5 the measurements were made on powder. A molten sample forms a very thin film, the height of which could not be measured by our optical microscope. The current from redox processes on this film was obscured by a large current from the oxygen reduction.

3. Results and discussion

3.1. Cu metal

The voltammogram of a copper metal sample is shown in Fig. 2. Two main oxidation (O1, O2) and reduction peaks (R1, R2) correlating with the two oxidation states of copper, Cu_2O and CuO, were recorded. A pre-peak O1′ exists just at the beginning of the first oxidation peak O1. Oxidation peak O2 overlaps to some extent with that of peak O1 and
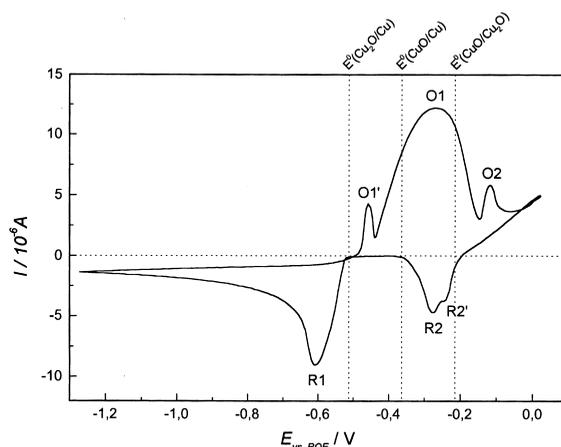

Fig. 2. Voltammogram of a copper metal sample at 700°C. ($\cdots$) Calculated equilibrium potentials for the reaction.

with an anodic current at more positive potentials. A second pre-peak R2′ is seen at the beginning of the reduction peak R2. At lower temperatures the separation of R2′ and R2 is improved. The potential scale on the x-axis has been corrected and is given versus the reversible oxygen electrode (ROE) at an oxygen partial pressure of 1 atm, following the procedure described in Ref. [3]. The equilibrium potentials of the reactions

$$2CuO \rightleftarrows Cu_2O + \tfrac{1}{2}O_2, \tag{1}$$

$$Cu_2O \rightleftarrows 2Cu + \tfrac{1}{2}O_2 \tag{2}$$

could be determined from the potential where the reduction and oxidation peaks start. In Fig. 2 the equilibrium potentials of reactions (1) and (2), calculated from thermodynamic data [6], are indicated by dotted lines for comparison. The measured and calculated potentials are listed in Table 1. The shape of the plot is very similar to the voltammograms obtained for pressed and sintered pellets of a mixture of CuO and Cu powder [2]. The observed pre-peak O1′ is smaller than reported in Ref. [2] and, in addition, we also detected a pre-peak R2′.

From a purely thermodynamic perspective only two oxidation and reduction processes, rate determined by diffusion processes, should occur related to the two existing stable oxides. Presumably, the formation of oxide scales on the metal surface is the origin of the appearance of pre-peaks. The presence

Table 1
Calculated and measured equilibrium potentials for the measurements on copper metal and Bi_2O_3

Temp. (°C)	vs. $p_{O_2} = 1$ atm					
	CuO/Cu_2O		Cu_2O/Cu		Bi_2O_3/Bi	
	$E^0_{calc.}$ (mV)	$E^0_{meas.}$ (mV)	$E^0_{calc.}$ (mV)	$E^0_{meas.}$ (mV)	$E^0_{calc.}$ (mV)	$E^0_{meas.}$ (mV)
550	−293	−200	−564	−557	−603	−437
600	−266	−212	−547	−541	−577	−452
650	−240	−195	−529	−523	−552	−424
700	−214	−158/−210[a]	−512	−507/−510[a]	−527	−414

[a] Values for the CuO powder sample.

of an insulating oxide layer invalidates the assumption of an inert electrode being necessary for the application of the equations for the current–voltage relationships, derived from voltammetric theory.

3.2. CuO powder

The results of measurements on CuO powder microsamples support this interpretation (Fig. 3). Probably because of the larger proportion of surface to bulk and the smaller sample mass the peaks are sharper and the pre-peaks disappear or are like spikes. Because of the rapid current increase of both the oxidation and reduction peaks, the equilibrium potential of the corresponding redox reaction can be resolved very accurately. The agreement of the calculated and the measured equilibrium potentials is within 4 mV (see Table 1). The charge under O1 and O2 should be the same for the oxidation of one

copper atom according to reactions (1) and (2) as well as for the reduction peaks if one assumes that in both reactions the whole sample mass is involved. The measured charges of the oxidation and reduction peaks are comparable in this experiment. This is not the case for the measurement on the copper metal.

3.3. V_2O_5 microsamples

The voltammograms of molten or powdered samples display the same shape as in Fig. 4. Measurements were performed only at temperatures below the melting point of V_2O_5 of about 670°C. The molten sample spreads over the surface and forms a very thin layer of V_2O_5. The currents due to reduction or oxidation on such a sample are very small and obscured by the oxygen reduction current even if the partial pressure is in the range $p_{O_2} \cong 10^{-6}$ atm. At least three oxidation O1–O3 and reduction peaks

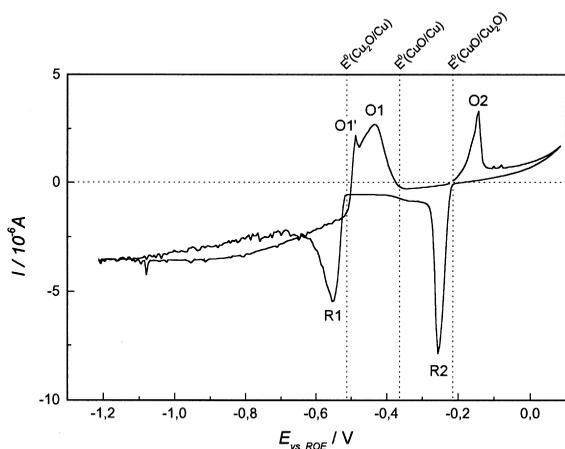Fig. 3. Voltammogram of a CuO powder microsample at 700°C. ($\cdots$) Calculated equilibrium potentials for the reaction.
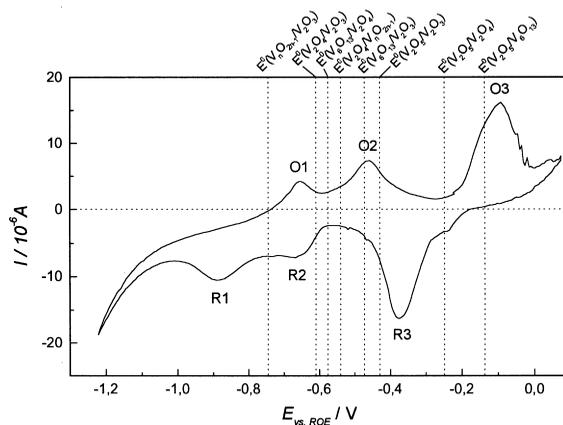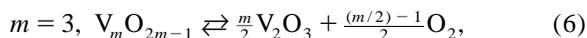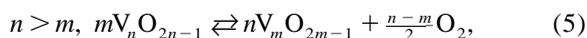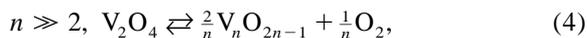

Fig. 4. Voltammogram of a V_2O_5 microsample at 650°C. ($\cdots$) Calculated equilibrium potentials for the reaction.

R1–R3 were observed. Sometimes a pair of very weak peaks was visible at more negative potentials than those for the peaks R1 and O1. Since the vanadium system includes a large number of stable oxides it is very difficult to propose a reaction route for our results. The calculated equilibrium potential [6] of some transitions is indicated by dotted lines. The most negative potential applied to the sample was about -1200 mV. This is within the stability range of V_2O_3. From a thermodynamic point of view the sample must be reduced to V_2O_3. From our TGA measurements on V_2O_5 in hydrogen [7] we know that V_2O_5 is reduced to V_2O_3 at temperatures not higher than 850°C. A possible reaction path for the electrochemical reduction of V_2O_5 to V_2O_3 is

$$V_2O_5 \rightleftarrows V_2O_4 + \tfrac{1}{2}O_2, \tag{3}$$

$$n \gg 2, \quad V_2O_4 \rightleftarrows \tfrac{2}{n}V_nO_{2n-1} + \tfrac{1}{n}O_2, \tag{4}$$

$$n > m, \quad mV_nO_{2n-1} \rightleftarrows nV_mO_{2m-1} + \tfrac{n-m}{2}O_2, \tag{5}$$

$$m = 3, \quad V_mO_{2m-1} \rightleftarrows \tfrac{m}{2}V_2O_3 + \tfrac{(m/2)-1}{2}O_2, \tag{6}$$

where V_nO_{2n-1} and V_mO_{2m-1} with $n,m > 2$ are the so-called Magnéli-phases which are a series of homologous compounds.

From the shape of the voltammograms it seems that a passive layer is not formed as in the case of copper and nickel. The current does not decrease rapidly immediately after a peak. The shape of the current peaks is symmetric. This might be an indication that diffusion is relatively fast in all kinds of oxides.

3.4. Bi_2O_3 microsamples

The reproducibility of the voltammograms of Bi_2O_3 powder or molten samples is poor. In many cases an irregular shape of the reduction current was observed (Fig. 5a). In Fig. 5b only one oxidation and reduction peak is visible. The equilibrium potential (see Table 1) obtained from voltammogram (a) does not agree with the calculated equilibrium potential [6] for the reaction

$$Bi_2O_3 \rightleftarrows 2Bi + \tfrac{3}{2}O_2. \tag{7}$$

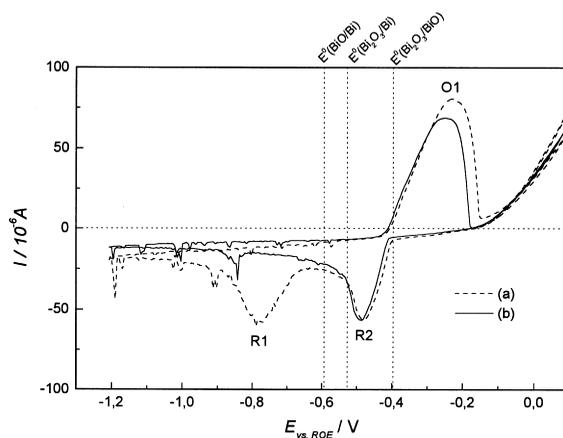The existence of other stable oxides at higher

Fig. 5. Voltammogram of a Bi_2O_3 microsample at 700°C. (a) First cycle, (b) second cycle. ($\cdots$) Calculated equilibrium potentials for the reaction.

temperatures is questionable. BiO is probably a metastable compound which decomposes into Bi and Bi_2O_3 at higher temperatures. The melting point of bismuth metal is 271°C.

Because we started the scan in the stability region of Bi_2O_3 and proceeded first in the anodic direction the sample should be in the fully oxidised state. In the following cathodic scan the reduction of Bi_2O_3 should lead to molten bismuth because of the high temperature. The reacting substances are not in the standard condition. This could influence the equilibrium potential and the shape of the reduction current. Another explanation for the irregular current shape is the formation of metastable BiO and its reduction at more negative potentials.

3.5. BICUVOX.10

For comparison, the voltammogram of BICUVOX.10, taken from Ref. [3], is shown in Fig. 6. It is not surprising that no agreement between the voltammogram of BICUVOX.10 and that of pure oxides is evident. The ternary oxide system is very complicated and reactions between the electrolyte or the platinum electrode may occur. Only two remarkable results will be discussed:

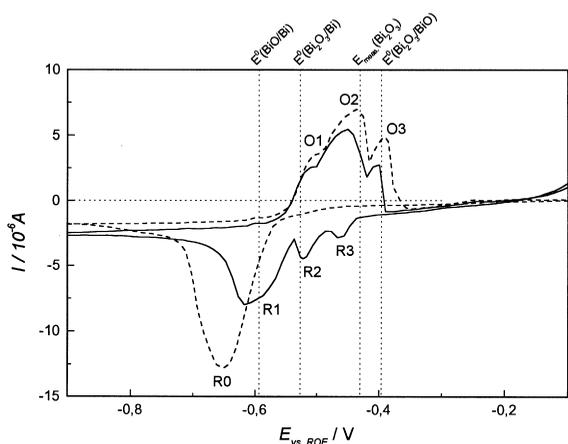- the coincidence of the onset potential of R0 with the *calculated* equilibrium potential of Bi_2O_3/Bi,

Fig. 6. Voltammogram of a BICUVOX.10 microsample at 700°C (from Ref. [3]). (- - -) first cycle; (———) second cycle. Dotted line (a) indicates the calculated equilibrium potential of the Bi/Bi_2O_3 electrode, and line (b) our measured value.

- the coincidence of the onset potential of R3 with the *measured* equilibrium potential of Bi_2O_3/Bi.

This is perhaps an indication that the stability of BICUVOX.10 against (complete!) reduction is determined by the stability of a kind of Bi_2O_3/Bi electrode where the Bi does not escape from the bulk. This behaviour was found in partly reduced Bi_2O_3/Y_2O_3 compounds [8]. In turn, if the sample is completely reduced, as it is in our experiment, part of the sample behaves like 'pure' Bi_2O_3 and 'free' bismuth.

4. Conclusion

Voltammetry on microsamples was used for the determination of the redox potentials of several metal oxides. The measured redox potentials of CuO microsamples agree very well with calculated values within 4 mV. This demonstrates the suitability of the method. A large difference between measured and calculated values was observed for Bi_2O_3. The reason for this disagreement cannot be explained. An electrochemical reaction path for the reduction of V_2O_5 to V_2O_3 has been proposed. A comparison between the voltammograms of Me_xO_y and that of BICUVOX.10 showed no agreement of any of the peaks. The reason for this might be an alloying with any of the involved substances, i.e. platinum, bismuth, vanadium and copper, or a chemical reaction with YSZ or the formation of new compounds between the oxides.

Acknowledgements

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