



Voltammetry on BICUVOX.10 microsamples

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Abstract

BICUVOX.10 ($\text{Bi}_2\text{Cu}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$) might be a very attractive material for use in oxygen sensors, fuel cells and oxygen separators. The electrochemical stability of BICUVOX.10 is an important factor for its future application. The electrochemical reduction and oxidation can be recognized very easily by the voltammetric technique. Our previous voltammetric measurements were made on 3-electrode cells like $\text{Pt}, \text{O}_2 | \text{BICUVOX.10} | \text{O}_2, \text{Pt}$ using $\text{BICUVOX.10} | \text{O}_2, \text{Pt}$ as reference electrode. This investigation showed a reduction of the material in the cathodic scan, followed by an oxidation peak in the anodic one. However, a quantitative elucidation of the reduction processes was not possible. The use of small samples in a cell of the arrangement $\text{Pt}, \text{Ar} | \text{sample} | \text{YSZ} | \text{Ar}, \text{Pt}$ allows to distinguish between different reduction steps during the negative sweep. The reference electrode was a platinum point electrode applied to YSZ. Because of the small size of a sample it can be reduced to a large extent at temperatures above 600°C . We found that the sample started to be reduced irreversibly below -570 mV against the reversible oxygen electrode in 1 atm O_2 during the first negative sweep. Only part of the reduced sample can be reoxidised during the next positive sweep. The subsequent cycles showed reversible reduction and oxidation of the residual oxides. © 1998 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

In the early seventies, Bi_2O_3 was found to exhibit a large oxygen ion conductivity [1] at a temperature above 730°C . Below this transition temperature the conduction is low and mixed (β -phase) or electronic (α -phase) [2]. By doping Bi_2O_3 with different oxides, the high temperature δ -phase (fcc) could be stabilized at lower temperatures.

More recently the compound $\text{Bi}_4\text{V}_2\text{O}_{11}$, which shows three structural phases (α , β , γ), was found [3] to have high ionic conductivity in the high temperature γ -phase. Discontinuous changes in con-

ductivity and three regions of different activation energies in the Arrhenius plot of the conductivity correspond to the three phases. The γ -phase shows a low activation energy of about 0.2 eV and a transference number of oxygen ions close to one. This phase was stabilized by substitution of part of the vanadium by other metals [4]. The oxygen ion conductor with the best known conductivity of this so-called BIMEVOX-family is BICUVOX.10 ($\text{Bi}_2\text{Cu}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$). The conductivity at 300°C is about two orders of magnitude higher than that of yttria stabilized zirconia (YSZ). Good conductivity at low temperatures is important but some other criteria must be fulfilled for an application too:

- low electronic conductivity,

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- electrochemical and mechanical stability under the given working conditions,
- low costs.

The existence of electronic conductivity is a restriction especially for sensors. Results obtained by different methods give indications that BICUVOX.10 is a mixed conductor with a dependence of the transference number on oxygen partial pressure or electrochemical potential. Measurements of the electronic conductivity by the Faraday efficiency method showed a decrease of the average oxygen transference number with increasing current density [5]. In fact, there is a disagreement of the measured voltage and the theoretical Nernstian voltage in an oxygen sensor based on BICUVOX. Polarization by the internal current at the interface of such a sensor is the reason for this deviation. Impedance measurements showed a smaller electrode polarization resistance at lower oxygen partial pressures. The cathodic currents measured in cyclic voltammetry are considerably higher for BICUVOX.10 than for YSZ when similar electrodes (point electrodes) were used [6]. The apparent active surface is about 100 times higher. It is likely that a change in oxygen stoichiometry or valence of any of the compounds occurs with cathodic polarization. This can introduce electronic conductivity which can explain a contribution of the electrolyte surface to the Faradaic reaction.

The redox stability range and electronic conductivity of some bismuth based electrolytes was determined by measurements of Takahashi et al., and Verkerk and Burggraaf [7–9]. Potentiometric measurements on partly reduced $\text{Bi}_2\text{O}_3\text{-Y}_2\text{O}_3$ samples revealed that Bi_2O_3 was reduced to Bi metal in atmospheres containing less than $10^{-13.1}$ atm P_{O_2} at 600°C. A potential relaxing experiment on BICUVOX.10 was applied by Iharada et al. [5]. After a reduction pulse the change of open circuit voltage was recorded. A redox stability limit between -0.3 V and -0.4 V with respect to the oxygen electrode in air at 600°C was determined which corresponds to $10^{-7.6}$ to 10^{-10} atm P_{O_2} . Our voltammetric measurements on large BICUVOX.10 samples in the cell $\text{Pt, O}_2|\text{BICUVOX.10}|\text{O}_2, \text{Pt}$ indicated also a reduction of the electrolyte at more positive cathodic polarization than expected for

Bi_2O_3 [6]. After a cathodic scan an anodic current peak appears in the positive scan. The peak height increases with lower partial pressure of oxygen in the atmosphere. From these measurements it was evident that a reduction of the material occurs, but the evaluation of quantitative results like thermodynamic data was not possible.

The redox stability range of the material can be determined quantitatively in a very gentle way by cyclic voltammetry on BICUVOX.10 microsamples. The advantage of this method is the easy identification of reaction steps which occur during the linear change of the electrode potential. Because of the smallness of the samples a reduction or oxidation step can be completed before the next reaction step starts. The results are compared with measurements available in literature and with thermodynamic data.

2. Experimental

The measurements were carried out in the temperature range between 600°C and 750°C in a fully automated set-up for which a detailed description is given in Ref. [10]. The data was acquired by a computer and stored on disc for later evaluation. The whole cell was kept in a special holder in a quartz glass tube which can be flushed with different gases. It consisted of a disk of yttria stabilized zirconia (YSZ) containing 8 mol% Y_2O_3 from Friatec. 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 covered one large side of the disc. On the opposite side of the disk a sample of BICUVOX.10 was attached in different ways, molten or pressed onto the YSZ disc, and contacted either with a small sheet of platinum or with a platinum tip.

The reference electrode (RE) was a small point of platinum paste on the same side of the YSZ contacted with a platinum tip (Fig. 1). If the RE, which works as an oxygen electrode, behaves reversible the potential is determined by the oxygen partial pressure in the ambient gas. The potential of such a platinum electrode is stable and reproducible within 10 mV between 500°C and 750°C [10,11]. The oxygen concentration must not be too high because

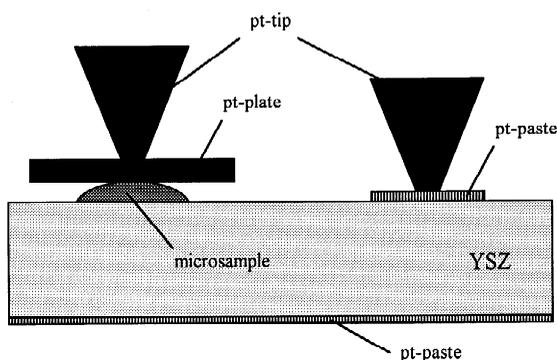


Fig. 1. Schematic diagram of the arrangement of the sample and electrodes. The size of the microsample is not drawn to scale.

the current from the parallel reaction of the O_2 reduction at the WE may hide the currents due to the reduction of the sample. In some experiments we used nitrogen/oxygen gas mixtures with 10^{-3} atm P_{O_2} . The advantage of the relatively high oxygen partial pressure is a known and well defined RE potential. Unfortunately the Faradaic currents from the oxygen reduction at the WE were too large. Nevertheless a stable residual oxygen partial pressure in the inert gas is important because of three facts:

- The sample must not be reduced by the low P_{O_2} before a measurement is performed.
- The potential of the RE must be stable during the time of an experiment even it is unknown.
- Oxygen ions must be supplied from the CE by reduction of O_2 during oxidation processes at the WE.

The use of argon or nitrogen with a purity of 99.999% was found to be a good compromise. The oxygen partial pressure was mainly determined by the inherent leakage of the setup. The potential of the RE is stable during one experiment which lasts 3 h to several days but may vary up to 200 mV between different runs after opening of the holder, depending on the tightness. For a determination of thermodynamic data the 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. Because the potential of the RE is unknown in our experiments it was

determined by an independent voltammetric measurement of the Ni/NiO system. For that purpose a pure nickel wire was used as WE and pressed on the YSZ. The result gives the potential of the RE in relation to the standard potential of the Ni/NiO electrode ($E_{vs.RE}^{Ni/NiO}$). The standard potential of the Ni/NiO electrode with respect to the ROE at 1 atm O_2 ($E_{vs.ROE}^{Ni/NiO}$) can be calculated from thermodynamic data available in literature. A correction of the potential scales of the measurements on BICUVOX.10 samples ($E_{vs.RE}^{Sample} \rightarrow E_{vs.ROE}^{Sample}$) was applied according to Eq. (1).

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

The accuracy of the measured potential of the Ni/NiO electrode was verified in an individual experiment. Scans with two different potential windows at several scan rates and temperatures were done. The first experiment involved a potential window of 800 mV with the E_0 of the Ni/NiO electrode at about -0.1 V with respect to the RE. The potential of the RE is controlled by the actual oxygen partial pressure in the chamber which is about 10^{-15} atm P_{O_2} in these experiments. The low partial pressure ensures that no significant reduction current of O_2 overlaps. The anodic reversal potential was $+0.3$ V, the cathodic one was -0.5 V.

In the following experiments with BICUVOX.10 samples this nickel wire was attached directly on the YSZ pellet acting as a second additional working electrode. A voltammogram on this nickel wire was made before and after a measurement without change of the temperature or configuration for checking the stability of the RE potential.

Disks of polycrystalline BICUVOX.10 samples were produced from analytical grade oxides in a procedure described previously [12]. Small pieces with a weight of less than $10 \mu\text{g}$ were cut from this material. The junction between the sample and the YSZ was made either by melting of the sample or by simple pressing it onto the YSZ disk. The volume of the molten samples was roughly determined by measuring the diameter and the height of the sample on the YSZ by optical microscopy. The weight was calculated from the volume and the density of the sample. This procedure gives more accurate results than the direct weighing of the sample attached on

the YSZ. For the samples which were only pressed at the YSZ pellet a determination of the weight was not possible.

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 700°C and kept for about one hour in 100% O₂. In addition three cycles from zero to +0.3 V and back to zero at 50 mV s⁻¹ were applied to the WE. After this procedure a temperature between 600°C and 750°C was set in 50°C steps and a measurement was performed. This was done for each temperature with a fresh sample. The first scan extended from zero against the RE to +0.3 V. Then a negative scan to -1.0 V was applied followed by a positive one back to zero. Three complete cycles were made in all measurements at a scan rate of 1 mV s⁻¹. The slow scan rate is necessary to enhance the sharpness of the peaks and to allow a complete reduction or oxidation of the sample during one cycle.

3. Results and discussion

Fig. 2 shows a cyclic voltammogram on Ni at 700°C. Nickel displays only one oxidation and reduction peak in the cyclic voltammogram.

The validity of the Eq. (3)– Eq. (7) given in the appendix can be established from the dependence of peak potentials and currents upon scan rate and temperature [13]. This was shown in literature for

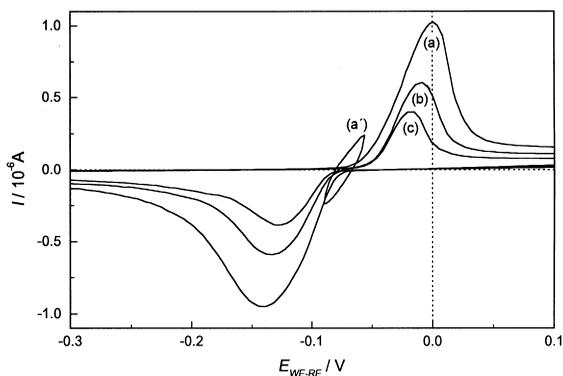


Fig. 2. Cyclic voltammogram for the Ni, Ar|YSZ interface at 700°C. The scan rate was (a) and (a') 20 mV s⁻¹, (b) 10 mV s⁻¹, (c) 5 mV s⁻¹. Reversal potentials of curve (a): -500, +300 mV, of curve (a'): -90 mV, -50 mV.

the nickel system with pressed Ni/NiO powders as electrodes. It was concluded that the electrode does not behave reversible, but the difference between the measured $E_{1/2}$ value from the standard potential E_0 was considered small [14].

In our case also a dependence of the peak potential and the peak current upon the scan rate was observed (Figs. 2–4). The assumption of a reversible reaction is not valid. The electrode changes with polarization and time due to oxide layer formation on the nickel surface. Therefore the electrode is not inert which is a possible explanation for the observed deviation from the theory.

$E_{1/2}$ was computed from these measurements according to Eq. (3). Around $E_{1/2}$ a cyclic volt-

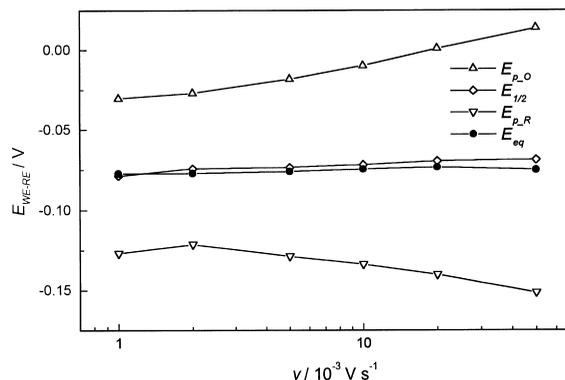


Fig. 3. Plot of the measured peak and E_{eq} potentials and the calculated $E_{1/2}$ at 700°C against the scan rate ν for the Ni, Ar|YSZ interface at 700°C.

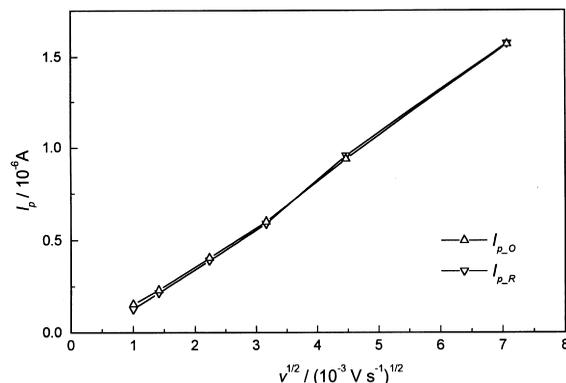


Fig. 4. Plot of the measured absolute values of the peak currents $I_{p,O}$ and $I_{p,R}$ against the square root of the scan rate ν at 700°C.

ammogramm was taken in which the electrode was polarized by ± 20 mV in the anodic and cathodic direction. After a correction for the double layer capacity current, the equilibrium potential E_{eq} was determined as the zero crosspoint of the sum of the anodic and cathodic current branches with the potential axis. This value is compared with the $E_{1/2}$ value in Fig. 3. The variation of the measured equilibrium potential E_{eq} with scan rate is less than 4 mV. The maximum difference between E_{eq} and $E_{1/2}$ is less than 8 mV. Therefore the $E_{1/2}$ value can be taken as E_0 with satisfying accuracy in the latter measurements.

The micrograph in Fig. 5 shows a sample of BICUVOX.10 molten on YSZ. The weight of this sample was computed by using the Eq. (2) for calculation of the volume of part of a sphere

$$V = \pi \cdot h \cdot \frac{3a^2 + h^2}{6} \quad (2)$$

where h is the height and a is the diameter of the base.

With a theoretical density of 7.84 g cm^{-3} a weight of $7 \mu\text{g}$ was determined. There is some uncertainty in the calculation of the mass. It might be overestimated because of the imperfect shape and the presence of holes and cracks in the sample.

The potential scale for the following measurements was corrected with respect to the ROE by

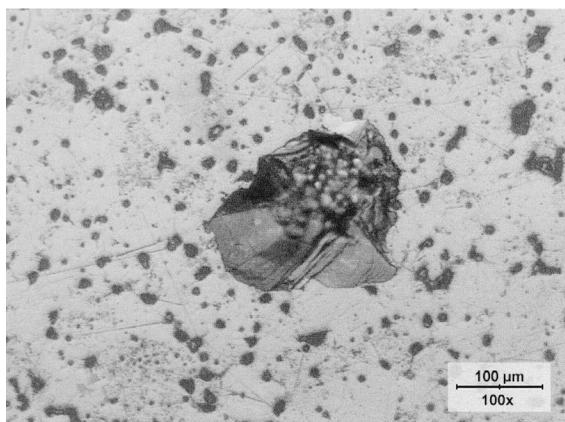


Fig. 5. Photograph of a molten piece of BICUVOX.10 on YSZ before a measurement. Small dark spots are caused by the pores in the YSZ. The base of the drop has an average diameter of $a = 189 \mu\text{m}$. The height is $h = 16 \mu\text{m}$.

measuring the $E_{1/2}$ for the Ni/NiO system before and after the measurement on BICUVOX.10 as mentioned in the experimental section. For these experiments the equilibrium potential of the Ni/NiO electrode with respect to the RE was -0.4 V to -0.6 V, which indicated an oxygen partial pressure in the chamber in the range of about 10^{-5} to 10^{-9} atm P_{O_2} . Actually there was some O_2 reduction current observed which overlapped with the current of the Ni/NiO electrode. A correction for the reduction current of the residual oxygen in the gas was applied by subtraction of a baseline.

Fig. 6 shows a cyclic voltammogram of a molten BICUVOX.10 sample. It represents the first run with a virgin sample. In the first cathodic sweep only a single peak (R0) arise. The charge of the peak was calculated by numerical integration of the data taking a baseline into account. The calculated charge of this peak ($Q_{R0} = 1.16 \text{ mC}$) corresponds to about 12% of the sample mass under the assumption that the oxide fractions of the sample were in the highest oxidation state and CuO is reduced to metallic copper, V_2O_5 to V_2O_3 and Bi_2O_3 to metallic bismuth.

It was not possible to reoxidise the sample completely in the anodic scan where three overlapping oxidation peaks have been recorded. The charge under the peaks O1–O3 is smaller than for the

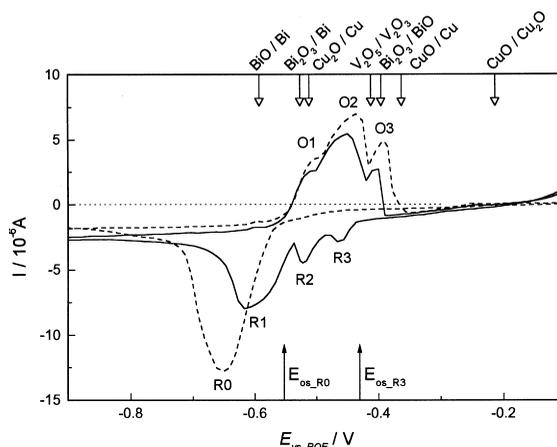


Fig. 6. Cyclic voltammogram for the Pt,Ar|BICUVOX.10|YSZ interface taken at 700°C at a scan rate of 1 mV s^{-1} . The weight of the sample was $7 \mu\text{g}$. Broken line for the first scan, solid line for the second scan. Arrows on the top mark the theoretical equilibrium potentials of some selected $\text{Me}_m \text{O}_n / \text{Me}_x \text{O}_y$ mixtures derived from thermodynamic data.

charge of the R0 peak ($Q_{O1-3} = 0.6 Q_{R0}$). In the following cathodic scan also three peaks arise obviously corresponding to the anodic ones. In the following scans the voltammogram remained unchanged indicating that an irreversible reduction occurred during the first cathodic scan.

Because of the irreversible reduction a determination of the equilibrium redox potential of BICUVOX.10 is difficult. The simple Eq. (3)–Eq. (7) are not valid for systems with irreversible charge transfer or with a following irreversible chemical reaction. Also the condition of plane diffusion in an infinite environment is not given in our case because of the use of microsamples. The relations are not only determined by the diffusion and charge transfer processes, but also by the fact that only a limited amount of active material is available. As the scan rate becomes smaller the peak becomes sharper and the peak potential moves towards the equilibrium potential. The peak potential becomes equal to the equilibrium potential for infinite small scan rate. This is in contrast to the theory where the difference between $E_{1/2}$ and E_{p_R} is given by Eq. (6) and independent of scan rate. E_{eq} of BICUVOX.10 cannot be determined in the same way as in the Ni/NiO system. Only an estimation of the onset potential of the reduction peak (E_{os_R}) is possible. The onset potential of the reduction peak in the first scan (E_{os_R0}) is different from them of the first reduction peak in the second scan (E_{os_R3}). E_{os_R0} is about 100 mV more negative compared with E_{os_R3} .

Arrows on the top are indicating the values for the equilibrium redox potential of some selected pure metal oxides calculated from their thermodynamic data in Fig. 6. The temperature dependence of the measured and the theoretical values is shown in Fig. 7. There is some agreement between E_{os_R0} of the reduction peak R_0 and the standard potential of the Bi_2O_3/Bi system [15]. E_{os_R3} or the $E_{1/2}$ of the peaks R3 and O3 respectively agree with the standard potential of the V_2O_5/V_2O_3 electrode or with them of the Magnéli phases V_3O_7/V_nO_{2n-1} ($2 < n < 9$) [16].

A full explanation of the redox peaks of the reduced sample is very complicated because of possible alloy formation with the electrode material or chemical reaction with YSZ. Alloying with the platinum contact is possible for all three components,

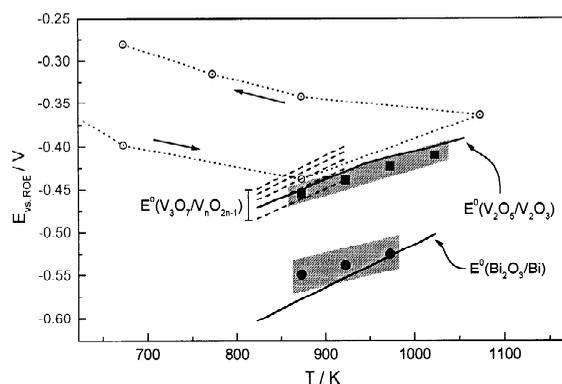


Fig. 7. Temperature dependence of the measured onset potentials E_{os_R0} (filled circles) and E_{os_R3} (filled squares) of BICUVOX.10. Shaded area: error bands. Lines: calculated equilibrium potentials of selected Me_mO_n/Me_xO_y mixtures. Open circles with dotted line: Redox potential according to [5], heating and cooling.

bismuth, vanadium and copper. Alloying or a chemical reaction will shift the equilibrium potential compared to that of the “free” redox reaction. This is the reason why a definite classification of the observed equilibrium potentials failed.

In potential relaxing experiments [5] a hysteresis of the redox potential between heating and cooling cycle was found. A comparison with our results (Fig. 7) suggests that this hysteresis is a result of an irreversible reduction of the sample. The observed plateaus are probably related to the fact that the irreversibly reduced sample is reoxidised in three distinct steps as in our measurements. In addition alloy formation with the electrode material has to be considered to have an influence on the measured values of the equilibrium potential.

4. Conclusion

Cyclic voltammetry on microsamples allowed the determination of the electrochemical stability range of BICUVOX.10 in a very convenient way. The reduction of the material is irreversible, maybe because of alloy formation with the electrode material or chemical reaction with the YSZ. A reconstitution of the original structure of BICUVOX.10 is not possible by electrochemical oxidation. This is probably only possible by long exposure to air at elevated temperatures.

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Appendix 1

The measurement of standard potentials is a substantial part of the work the intention of which is the estimation of the electrochemical stability range of the sample. The determination of the standard potential by cyclic voltammetry is a complex procedure compared to stationary potentiometric measurements. An explicit solution for the computation of the standard potential on the basis of voltammograms is only possible for specific conditions. According to voltammetry theory the mean value $E_{1/2}$ between the reduction and oxidation peak potential E_{p_R} and E_{p_O}

$$E_{1/2} = \frac{E_{p_O} + E_{p_R}}{2} \quad (3)$$

is given by

$$E_{1/2} = E_0 + \frac{RT}{nF} \cdot \ln \left(\sqrt{\frac{D_r}{D_0}} \right) \quad (4)$$

E_0 is the standard potential and D_r and D_0 are the diffusion coefficients for the reduced and oxidized species. This equation is valid for diffusion controlled systems with reversible charge transfer reaction and diffusion of the active species in a plane and infinite environment with some specific boundary conditions, i.e. the absence of the reduced species at the start of the scan. Under the assumption that the diffusion coefficients D_r and D_0 are equal, $E_{1/2}$ is the standard potential E_0 of the redox reaction. The anodic and cathodic peak potentials E_{p_O} and E_{p_R} are given by

$$E_{p_O} = E_{1/2} + 1.109 \cdot \left(\frac{RT}{nF} \right) \quad (5)$$

$$E_{p_R} = E_{1/2} - 1.109 \cdot \left(\frac{RT}{nF} \right) \quad (6)$$

The peak current I_p is given by

$$I_p = 0.4463 \cdot A \cdot c_0 \sqrt{\frac{(nF)^3}{RT}} \cdot D \cdot v \quad (7)$$

in which A is the electrode surface, D the diffusion coefficient and c_0 the concentration of the reacting species in the infinite and v the scan rate.

In systems with quasi-reversible charge transfer a dependence of the peak potential on scan rate will be expected. If the charge transfer reaction is very slow (irreversible) compared to the diffusion process a strong shift of the peak potential will be observed. At moderate polarization around the standard potential E_0 the charge transfer reaction predominates.

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