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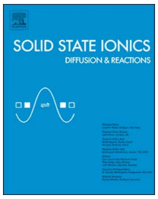

On the mixed ionic and electronic conductivity in polarized yttria stabilized zirconia

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ABSTRACT

Electric transport in oxides with mixed conduction, being exposed to dc electric fields and being placed between blocking electrodes is discussed and exemplified for yttria stabilized zirconia (YSZ). This is relevant for cases of large current densities in solid oxide fuel cell (SOFC), solid oxide electrolysis cells (SOEC) and during flash sintering of oxide powders. In the present study equilibrium of defect reactions is not attained in the presence of blocking electrodes leading to a continuous generation of holes in p-regions and electrons in n-regions feeding the external current. In the remaining region between n- and p-region ion conduction is dominant. Thus a p-i-n junction is formed. The electronic species may be continuously generated by reaction with gaseous oxygen or by the creation and annihilation of single-charged vacancies. For both cases current voltage-relations are derived by assuming that the gradient of the chemical potential of double-charged vacancies is reduced below its value given by a zero electrochemical potential. The reduction is introduced as a consequence of the Le Chatelier Principle, which requires reactions to occur, which counteract the accumulation and depletion of double-charged vacancies by the applied electric field and corresponding deviations from charge neutrality. Scenarios are discussed where electrons and holes recombine with a concomitant emission of light. This explains why the spectrum of the emitted light deviates from that of black body radiation for both examples of flash sintering and the Nernst glower.

1. Introduction

Under ambient oxygen pressures most oxides have a large band gap in their electronic structure and, therefore, exhibit negligible electronic conductivity. However at high temperatures vacancies in the oxygen sublattice give rise to ionic conductivity. Yttria doped zirconia or yttria stabilized zirconia (YSZ) is one of the examples containing a large fraction of structural vacancies. Yttria forms a solid solution in zirconia up to high concentrations [1]. In this solid solution of oxides the tetravalent zirconium is partly substituted by trivalent yttrium and vacancies are generated in the oxygen sublattice in order to maintain charge neutrality. Thus the concentration of the vacancies can be very high and allow vacancies to move through the material. Then YSZ becomes a solid electrolyte and is used in solid oxide fuel cells (SOFC) and in solid oxide electrolysis cells (SOEC) [2–4]. Besides ions, electrons and holes contribute to the conductivity of YSZ. Electrons are formed at low oxygen pressures by a point defect reaction giving rise to n-type conduction [5–9], the relevant reaction in Kröger-Vink's notation is

$$O_O^x \rightarrow \frac{1}{2}O_2 + V_O^{\bullet\bullet} + 2e', \tag{1}$$

where $O_O{}^x$ refers to oxygen on anion lattice sites and $V_O{}^{\bullet\bullet}$ are double-charged vacancies on the same sublattice and electrons being placed in the conduction band. Eq. (1) being reversed leads to hole generation expressed by the following equation

$$V_O^{\bullet\bullet} + \frac{1}{2}O_2 \rightarrow O_O^x + 2h^{\bullet}, \tag{2}$$

where electrons from the valence band are used leaving holes behind. At dynamic equilibrium the individual forward and backward rates in Eqs. (1) and (2) have to be equal with electrons and holes annihilating each other by the reaction

$$e' + h^{\bullet} = nil \tag{3}$$

until their equilibrium concentrations are reached. With decreasing oxygen pressures Eq. (2) predicts, that less holes are produced with a concomitant increase of the concentration of electrons as the law of mass action requires for reaction in Eq. (3). Finally at a corresponding low pressure the electrons surpass the contributions of vacancies to

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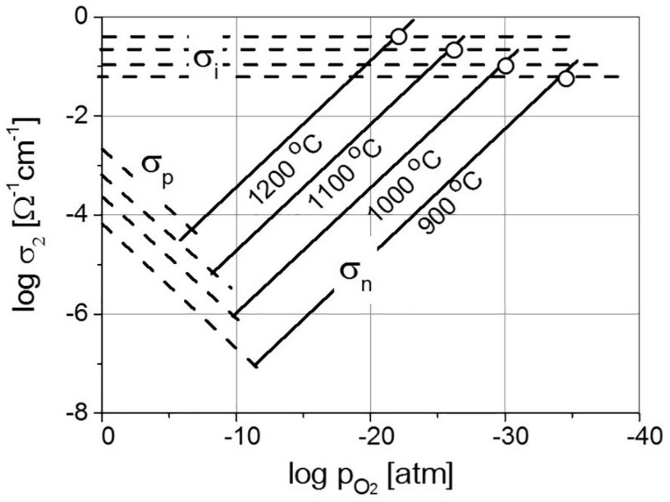

Fig. 1. Measured partial conductivities of YSZ as reproduced from Ref. [6] are shown at different temperatures as a function of the surrounding oxygen partial pressures (σ_2 is the partial ionic conductivity, σ_p and σ_n the one of holes and electrons). Similar values are obtained by others [5]. Open circles mark the partial pressures where electronic and ionic conductivity are equal.

conductivity and the YSZ becomes a n-type conductor. At increasing values of oxygen pressures the concentration of holes increases with a decreasing electron concentration and finally a transition from ionic to p-type conduction occurs. This has been experimentally proven in various studies [5,6]. The corresponding measurements of ionic conductivity σ_2 were performed at low dc-electric fields of the order of mV/cm or low ac-electric fields, in order to minimize or avoid polarization of YSZ. Under these conditions ionic conductivity prevails in a wide range of oxygen pressures as shown in Fig. 1. The term ionic conductivity will be used in this study despite the fact that vacancies are the moving charge carriers.

However it has been shown recently by Masao and West [7], that electronic conductivity in YSZ dominates at high dc-electric fields of 5 to 100 V/cm in air and at temperatures of 200 to 700 °C where for low dc-electric fields electronic conductivity is negligible. This different behavior was interpreted by the creation of single-charged oxygen ions. In a different experiment [10] with an electrochemical cell Ni/YSZ/Ni composed of a 2 mm thick disc of single crystalline 10YSZ between two nickel electrodes a constant current of 40 mA/cm^2 was passed through the electrolyte at 1200 K in vacuum (residual pressure: 10^{-3} Pa). The ionic part of the current caused the formation of NiO on the positive electrode whereas Ni_5Zr was formed at the negative electrode. The charge necessary for the formation of the NiO and the Ni_5Zr was about the same, but corresponded to 3% of the total electric charge only for a dc-field of 10 V/cm [10].

Besides applications in electrochemical devices, YSZ is also widely used as a structural material. For this purpose various shapes of the material are obtained by sintering oxide powders at elevated temperatures. As shown recently [11], the sintering process can be accelerated by applying electric fields during the compaction process. For very large electric fields a sudden increase of the current occurs after an incubation time and under potentiostatic control [12,13]. The current run-away is accompanied by emitting light with high intensity giving rise to the name flash sintering [14–16]. Whether the sudden current increase is caused by the onset of electronic conductivity or simply by Joule heating due to increasing ionic currents, is under debate [17,18].

The analysis of mixed ionic and electronic conduction is often based on the pioneering work of Carl Wagner [19–21] describing equilibrium of defect reactions with the electrochemical potentials η_i of the participating defect i. This was applied to YSZ [5,6] yielding for Eq. (1)

$$\mu_{O_O^x} = \frac{1}{2}\mu_{O_2} + \eta_{V_O^{\cdot\cdot}} + 2\eta_{e'}, \tag{4}$$

where for the neutral species the electrochemical potential reduces to the chemical potential. For a constant composition of YSZ the potentials of $O_O{}^x$ remains constant and, therefore, changes of oxygen pressure p_{O_2} or μ_{O_2}, respectively lead to changes of the electrochemical potential of vacancies and electrons. The latter quantity is the Fermi level of electrons, which then can be moved up and down either in the conduction band or in the valence band leading to n- or p-type conduction, respectively. With μ_{O_2} depending linearly on $\ln p_{O_2}$ and $\mu_{e'}$ on $\ln c_e$ (c_e being the concentration of electrons in the conduction band) the slope of $-1/4$ in Fig. 1 is explained, if the electronic conductivity is proportional to c_e [5,6].

In an electric field the charged species are moving and Hebb [22] and Wagner [21] assumed for the mixed conductors AgBr and Ag_2S that a steady state is attained with the gradients of the electrochemical potentials of ions to be zero. Schmalzried [23] pointed out that under these conditions internal reactions or reactions at the electrode/electrolyte-interfaces occur. Maier [24a,b] proposed the general concept of conservative ensembles including internal reactions with valence changes of moving ions and vacancies. In addition, he pointed out how blocking and/or reversible electrodes for either electrons or ions will change the voltage/current-relationship.

Choudhury and Patterson [25], Jacobsen and Mogensen [26] and Näfe [27] treated n- and p-type conduction in YSZ based on Eqs. (1) and (2). In all studies a gradient of the partial pressure of oxygen was evaluated. In order to maintain the related changes of pressure in steady state no exchange with oxygen from the surrounding atmosphere is allowed. The molecular oxygen needed to generate electrons and holes has to be ab- or desorbed from reversible electrode. This is different to Wagner's [20,21] and Hebb's [22] approach treating electron and silver ion production by the reactions

$$Ag_{Ag}^x \to Ag_i^\bullet + e', \tag{5}$$

where gradients of all species could sustain in the solid electrolyte by an internal reaction. Different to the treatment by Choudhury and Patterson [25] and others [26,27] exchange with environmental oxygen is allowed in the present study. Also different to a study by Reiss [28] for compounds with small deviations from stoichiometry the gradient of the chemical potential of the ions will not be zero. The cells used in references [21] to [28] consist of either two reversible or one reversible with one blocking electrodes.

Two blocking electrodes are used in order to determine the intrinsic electronic conductivity of the mixed conductor [22]. It is a major goal of this study to demonstrate that the electronic conductivity can be increased after an incubation time by two types of reactions generating electrons and holes. One of these types are the reactions in Eqs. (1) and (2) with gaseous oxygen provided by the environment. The electrons in n-type regions are generated continuously via Eq. (1) and holes in p-type regions via Eq. (2). Between n- and p-type regions a region with dominant ionic transport is required for avoiding a divergence of current. Molecular oxygen being generated in the n-region according Eq. (1) is consumed in the p-region via Eq. (2). Thus an external reaction at the electrolyte/gas-phase is controlling defect reactions.

A second type of reaction may play a role, if molecular oxygen is absent. Then electronic conductivity will be explained by the formation and transport of single-charged vacancies, which in Maier's concept [24a,b] can be formally treated with an individual diffusivity. In order to obtain analytical expressions for current and voltage simplifying assumption were made for the gradients of chemical potential of double and single-charged vacancies. Consequences of the models regarding the attainment of steady state and the emission of light are discussed at the end of this study.