MIXED IONIC-ELECTRONIC CONDUCTION IN HT_cS

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INTRODUCTION

Application of HT_cS materials as thin-film electrodes in solid state electrochemical systems, like solid oxide fuel cells (SOFC) and sensors, at elevated temperatures is a distinct possibility, provided that sufficient stability and electronic conductivity can be maintained. In addition, for these applications, HT_cS materials need to exhibit also some oxygen ion conduction at the temperatures of operation. From the group of ceramic HT_cS we have selected $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, 1, $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$, 2, and $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, 3, for detailed study. These materials have been shown to exhibit variable stoichiometry in the oxygen sublattice which can be related with ionic conduction at elevated temperatures¹⁻³.

For 1 oxygen stoichiometry and ordering have been the subject of thorough investigations. Oxygen ions in the CuO layer, common to the two barium-containing cubes in the 1 structure are the most loosely bound. These are the oxygen ions which disorder first on heating. Order-disorder phenomena in the oxygen sublattice are accompanied by loss of oxygen⁴. Schwartz et al.² have shown that the oxygen content of 1 is reduced at room temperature by electrochemical reduction in a propylene carbonate tetrabutylammonium perchlorate electrolyte. O'Sullivan and Chang³ have used a solid-state oxygen concentration cell, comprising 1 and sputtered Au as electrodes, and yttria-stabilized zirconia (YSZ) as the solid electrolyte. Using this cell, it was possible to electrochemically drive oxygen into and out of the 1 electrode. The diffusivity of oxygen in 94% dense 1 was estimated to be $\sim 5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ at 550 °C.

The effect of loss of lattice oxygen on the electrical properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ has been studied by Fiory et al.⁵. These authors demonstrate that this loss accounts for the sharp rise in electrical resistivity at $T > 400^\circ\text{C}$, since the increase of x with temperature causes the density of electronic states to decrease, and the elastic scattering rate due to oxygen vacancy order to increase. Similar observations were reported by Tu et al.⁶. They relate the resistivity increase, as measured in He as ambient, to effusion of oxygen. The rate of diffusion is assumed to be limited by reactions at the solid-gas interface.

In these studies, d.c. measurements are used with electrodes that are blocking to ionic currents, and ohmic for electronic charge carriers. Hence, the reported resistivity variations are to be related to the majority charge carriers in this oxide. To obtain the ionic conductivity in 1 a different type of electrode is required.

Sofar, little is known about the mixed ionic-electronic conductivity, the stability and the electrocatalytic properties of the new ceramic superconductors at high temperatures. These materials may replace, for instance, the current state-of-the-art cathode material $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ in SOFC reactors. This cathode material is responsible for the largest polarisation loss in the Westinghouse SOFC design.

We have studied ionic transport in 1-3, using a solid-state electrochemical cell, comprising ionically reversible $\text{Pt}(\text{O}_2)/\text{YSZ}$ electrodes which are blocking for electronic charge carriers, and the ceramic superconductor as a mixed-conducting solid electrolyte. Both a.c. impedance and d.c. polarization measurements have been performed. Part of the work on 1 has already been published¹.

EXPERIMENTAL

Ceramic superconductors 1-3 have been prepared by solid-state reactions, using as starting materials Y_2O_3 (Ventron, 99.99%), Eu_2O_3 (Ventron, 99.9%), La_2O_3 (Ventron, 99.9%), SrCO_3 (Merck, 99%), BaCO_3 (Merck 99%) and CuO (Ventron). Stoichiometric amounts of the reactants were thoroughly mixed, pressed into pellets (5 kbar) and subsequently fired. For 1 firing conditions are 950°C for 16 hours in air. After grinding the pellets of 1 and pressing new pellets, these were sintered in oxygen at 950°C for another 16 hours. The temperature was then

Figure 1. Impedance spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ in different oxygen ambients. Frequency range 0.1 Hz to 65 kHz.

lowered to 400 °C, and the pellets were kept in oxygen at this temperature for 12 hours.

For 2 firing conditions are 16 hours at 900 °C in air, regrinding and pressing, and subsequently sintering for 17 hours at 950 °C in oxygen. The sintered pellets were then kept at 450 °C for 10 hours. For 3 solid state reaction was achieved at 1100 °C for 17 hours in air. Following the procedure described for 1 and 2, sintering took place at 1100 °C for 18 hours in oxygen.

X-ray diffraction revealed 1 and 2 to have the orthorhombic structure, and 3 the tetragonal structure. The critical temperatures are 92 K (1), and 23 K (3). $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$ did not exhibit a Meissner effect at liquid nitrogen temperature.

The ionic transference numbers were studied with the cell (air)Pt/YSZ/mixed conductor, $\text{HT}_c\text{S}/\text{YSZ}/\text{Pt}(\text{air})$. Zirconia, stabilized with 8 mole percent (m/o) yttria (Gimex) was used in combination with Pt as the ion-reversible electrode. Further details have been reported by Vischjager et al.¹. The small-signal a.c. response of this cell arrangement was recorded using a computer-controlled Solartron 1250 Frequency Response Analyser, in combination with a Solartron 1286 Electrochemical Interface. A Marquardt non-linear least-squares parameter estimation for complex data has been used for the analysis of the admittance and impedance (immittance) spectra.

Results and Discussion

The small-signal a.c. response of 1, 2 and 3 is presented in Figure 1.

The response data could be fitted to equivalent circuits $R_1W_1pR_2sW_2p$ for 1, and 2, and $R_2W_2pR_{d1}C_{d1}psR_b s$ for 3. Here p stands for parallel and s for series. The equivalent circuits are presented in Figure 2.

A detailed analysis of the immittance spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ has been reported before¹. The equivalent circuit for 1 and 2 comprises the bulk ionic conductivity (R_2^{-1}), a grain boundary polarization effect of oxygen ions (R_1W_1p), while the parallel branch representing the electronic conductivity is manifested by a Warburg impedance only. The electronic resistivity in series with the Warburg impedance is extremely small, and does not show up in the immittance analysis, and hence the equivalent circuit.

The results for 3 reveal grain-boundary polarization not to occur in this material. The part $R_{dl}C_{dl}pR_b$ in the equivalent circuit for 3 is to be related with the $(O_2)Pt/YSZ$ electronically blocking electrodes. Ideally, the small-signal a.c. response of the cell $(O_2)Pt/YSZ/Pt(O_2)$ can be modelled with the equivalent circuit $R_{dl}C_{dl}pR_b$ ¹. R_{dl} and C_{dl} represent a Faraday impedance and a double layer capacitance,

Figure 2. Equivalent circuits for the cells $(O_2)Pt/YSZ/HT_cS/YSZ/Pt(O_2)$

respectively, at the $(O_2)Pt/YSZ$ interface, while R_b represents the bulk ionic conductivity of YSZ. In several instances, C_{dl} needs to be replaced with a constant-phase element ϕ having an admittance of the form $Y_\phi = k(i\omega)^\alpha$ with $0.5 < \alpha < 1$. This can often be related with current

inhomogeneities, which occur in polycrystalline samples. The ionic conductance (R_2^{-1}) of 1, 2 and 3 is plotted as specific ionic conductivities in an Arrhenius plot of $\log \sigma T$ vs T^{-1} (Figure 3).

The ionic conductivities are about a factor of 10^2 to 10 smaller than that of YSZ (8 m/o) in the temperature region 415 to 780 °C, indicating that oxygen ion conduction in these HT_cS materials is remarkably high.

Figure 3. Temperature dependence of the bulk ionic conductivity of 1, 2 and 3.

The conductivity activation enthalpies are 1.51 eV (1), 0.93 eV (2) and 1.27 eV (3). The numerical values for R_2 as obtained from fitting the impedance spectra in Figure 1 are presented in Table 1 along with the values for the specific electronic resistivity of these materials. From the respective ionic conductivities, the oxygen ion transference numbers t_i have been calculated, and included in Table 1.

Table 1				
HT _c S	T(°C)	R_2 (kΩ)	R_{e1} (Ωm) ⁷	t_i
YBa ₂ Cu ₃ O _{7-x} (air)	617	1	1.3×10^{-3}	7.28×10^{-7}
EuBa ₂ Cu ₃ O _{7-x} (O ₂)	572	2	-	5.6×10^{-7}
La _{1.85} Sr _{0.15} CuO ₄ (O ₂)	515	30	2.4×10^{-3}	2.0×10^{-7}

In the case of $\tilde{2}$ we have estimated the transference number by assuming $R_{el}(\tilde{1}) = R_{el}(\tilde{2})$.

For $\tilde{1}$ the transference numbers vary from 2×10^{-7} to 8×10^{-6} in the temperature range 500 to 625 °C. The present data for $\tilde{1}$ have been used to calculate the oxygen ion diffusion coefficient. At 503 °C $\sigma(V_O^{\cdot\cdot})$ of $\tilde{1}$ has the value $4 \times 10^{-5} \text{ S cm}^{-1}$ in air. The oxygen ion vacancy concentration at 500 °C is $5 \times 10^{21}/\text{cm}^3$ in air. For the mobility of the oxygen ion vacancies we then obtain $\mu(V_O^{\cdot\cdot}) = 2.5 \times 10^{-8} \text{ cm}^2/\text{Vs}$. With the Einstein relation $\mu/D = q/kT$ results for $D(V_O^{\cdot\cdot})$ the value $1.67 \times 10^{-9} \text{ cm}^2/\text{s}$ in air. For the tracer diffusion coefficient the value $10^{-10} \text{ cm}^2/\text{s}$ ($\text{PO}_2 = 1 \text{ atm}$, $T = 500 \text{ °C}$) was reported. With regard to chemical diffusion coefficient data the present value is in between these and the tracer diffusion coefficient.

In Figure 4 we have plotted the temperature dependence of the non-stoichiometry parameter x as obtained from the literature⁷. The variation of x in the orthorhombic phase reveals an activation energy of 0.22 eV, which is far below the conductivity activation enthalpy of 1.51 eV for $\tilde{1}$. We are, therefore, inclined to believe, that the present ionic conductivity measurements are not dominated by the loss of oxygen of $\tilde{1}$, and hence can be used to calculate diffusion coefficients.

Figure 4. Temperature dependence of x as calculated from ref. 7.

Usually, chemical diffusion coefficients are obtained by recording conductivity changes upon changing the ambient from air to oxygen. These

diffusion coefficients are apparent diffusion coefficients which should be analysed using ambipolar diffusion models. In general, such apparent diffusion coefficients are larger than diffusion coefficients calculated from conductivity data.

The present study indicates that $(O_2)Pt/YSZ$ electrodes effectively block electronic currents at the YSZ/HT_cS interface, and hence can be used to determine the ionic transference numbers in HT_cS materials. Further research is being carried out on $La_{2-x}M_xCuO_4$ ($M = Sr, Ba$).

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