Solid State Ionics 40/41 (1990) 810–814
North-Holland

IONIC CONDUCTIVITY OF CERAMIC SUPERCONDUCTORS

D.J. VISCHJAGER, A.A. van ZOMEREN, J. SCHOONMAN
Delft University of Technology, Laboratory for Inorganic Chemistry, Julianalaan 136, 2628 BL Delft, The Netherlands

and

I. KONTOULIS, B.C.H. STEELE
Imperial College, Department of Materials, London SW7 2BP, UK

The oxygen ion conductivity of $YBa_2Cu_3O_{7-x}$ (YBCO), $YBa_{1.99}K_{0.01}Cu_3O_{7-x}$ (YBKCO) and $Bi_{0.7}Pb_{0.3}SrCa_{1.8}Cu_2O_{8+x}$ (BPSCCO) has been studied with impedance spectroscopy in the temperature range 650–1150 K in oxygen using semiblocking electrodes based on YSZ (8 m/o), or $Bi_{1.75}Sm_{0.25}O_3$, which are reversible for oxygen ions and blocking for electronic charge carriers. With these electrodes oxygen conduction in Ag was studied to verify the reliability of the present solid state electrochemical technique. The small signal ac response has been modelled with equivalent circuits yielding the temperature and composition dependence of the ionic conductivity. The oxygen ion conductivity as obtained for Ag corresponds reasonably well to the conductivity calculated from reported oxygen flux data in Ag.

1. Introduction

High temperature studies of the electrical transport properties of the HT_cS materials can be divided into electronic and ionic conductivity studies. Usually the electronic conductivity is determined by the Van der Pauw method [1], whereas the ionic conductivity can be determined by ac impedance spectroscopy with a solid state electrochemical cell of the type

$$\mathrm{Pt(O_2)}\left|\begin{array}{l}\text{oxide solid:}\\ \text{electrolyte}\\ t_{O^{2-}}=1\end{array}\right|\begin{array}{l}\text{mixed conductor:}\\ t_{el}+t_{O^{2-}}=1\\ \end{array}\left|\begin{array}{l}\text{oxide solid}\\ \text{electrolyte:}\\ t_{O^{2-}}=1\end{array}\right|\mathrm{Pt(O_2)} \qquad \mathrm{(I)}$$

as has been shown by Vischjager et al. [2–4]. Here $t_{O^{2-}}$ represents the transference number for oxygen ions, and t_{el} that for electronic charge carriers. In this cell arrangement the semi-blocking $Pt(O_2)$ oxide solid: electrolyte electrodes are blocking for electronic charge carriers and reversible for oxygen ions.

In this paper we report on the oxygen ion conductivity of three ceramic superconductors: $YBa_2Cu_3O_{7-x}$ (YBCO), $YBa_{1.99}K_{0.01}Cu_3O_{7-x}$ (YBKCO), and $Bi_{0.7}Pb_{0.3}SrCa_{1.8}Cu_2O_{8+x}$ (BPSCCO) as obtained with cell arrangement (I). In addition, cell (I) with Ag replacing the mixed conductor was studied in order to verify the reliability of the present solid state cell. Oxygen is known to diffuse rapidly in silver. As protective oxide solid electrolytes YSZ (8 m/o), and $Bi_{1.75}Sm_{0.25}O_3$ have been employed.

As the awareness has grown that rewarding short term applications of the HT_cS materials may be far from those anticipated, the search for alternative uses has emerged. The occurrence of mixed ionic and electronic conductivity in these HT_cS materials at elevated temperatures opens up the possibility of utilizing them as oxidation catalysts, oxygen sensor materials, and electrodes in solid state electrochemical devices, like solid oxide fuel cells (SOFC). Our studies are focused on applications of the latter type.

2. Experimental aspects

The synthesis of the ceramic superconductors and protective electrolytes has been carried out by solid state reactions of high-purity metal oxides. YSZ (8 m/o) was obtained also commercially from Gimex (The Netherlands). The samples have been checked by X-ray diffraction. Except for the Bi-HT_cS compound, single phase materials were obtained. The Bi-compound consisted of the 2212 and 2223 phases.

YBCO of 0.26 cm thickness was provided on both sides with YSZ pellets of 0.24 cm thickness, which had been sputtered with Pt on one side, while YBKCO of 0.24 cm thickness was provided with single-side Pt sputtered YSZ (Gimex) of 0.05 cm thickness. For BPSCCO of 0.28 cm thickness single-side Pt sputtered $Bi_{1.75}Sm_{0.25}O_3$ was employed as the semi-blocking electrode. The Pt electrodes were sputtered with an Edwards Sputter Coater S150 B.

The HT_cS materials exhibited different porosities, i.e. 11% (YBCO), 37% (YBKCO) and 35–40% (BPSCCO).

The small-signal ac responses of the following cells were recorded in the temperature range of 650 to 1150 K using 1 atmosphere oxygen as ambient:

$Pt(O_2)/YSZ/YBCO/YSZ/Pt(O_2)$, (II)

$Pt(O_2)/YSZ/YBKCO/YSZ/Pt(O_2)$, (III)

$Pt(O_2)/Bi_{1.75}Sm_{0.25}O_3/BPSCCO/$
$Bi_{1.75}Sm_{0.25}O_3/Pt(O_2)$, (IV)

$Pt(O_2)/YSZ/Ag/YSZ/Pt(O_2)$, (V)

$Pt(O_2)/Bi_{1.75}Sm_{0.25}O_3/Ag/$
$Bi_{1.75}Sm_{0.25}O_3/Pt(O_2)$. (VI)

The admittance spectra were recorded using a computer controlled Solartron 1250 frequency response analyser in combination with a Solartron 1286 electrochemical interface in the frequency range 1–65.000 Hz. A complex non-linear least squares method has been used to fit the measured frequency dispersions of the solid state cells to an equivalent circuit description. An integrated software package was used, involving coordinated data storage, graphical presentation, and a Marquardt non-linear least-squares parameter estimation of complex data.

In order to check our method to determine oxygen ion conduction of mixed conductors with impedance spectroscopy on cells (II) to (IV), cells (V) and (VI) were studied.

3. Results and discussion

Fig. 1 presents a representative impedance spectrum of cell (III). Similar spectra were obtained with the other cells. The impedance spectra of the cells with YBCO and YBKCO as mixed conductor, and cell (V) could be modelled with the equivalent circuit R_1Q_1 pR_2Q_2 psR_3s. The equivalent circuit R_1Q_1 pQ_3s was found to fit the small-signal ac response of the cells (IV) and (VI). The equivalent circuits are presented in fig. 2. Here s stands for series and p for parallel.

In the equivalent circuits R_1 and R_2 represent Faradaic processes at the interfaces $Pt(O_2)/YSZ$ and YSZ/YB(K)CO. These interfaces are represented by the constant phase elements Q_1 and Q_2. R_3 comprises the sum of the bulk ionic resistivities of YSZ and the mixed conductor. Q_3 has a very small phase angle, i.e. 0.02–0.04, and is therefore interpreted as the bulk ionic conductivity of BPSCCO. The distributed character of this resistivity may be ascribed to current inhomogeneities as a result of the presence of two phases, i.e. 2212 and 2223. In comparison to the response data and the equivalent circuit modelling of cells (II) and (III), it seems that neither the polycrystalline character, nor the porosity of the samples can cause the distributed character of Q_3.

The assignment of the equivalent circuit elements is based on impedance data for cells with different interface geometries and interface roughnesses. Details will be published in a forthcoming paper [5]. The equivalent circuit for cell IV does not include R_1Q_1 p_1 because the interface kinetics at the $Pt(O_2)/Bi_{1.75}Sm_{0.25}O_3$ interface are fast compared to $Pt(O_2)/$YSZ.

From impedance spectra of the cells Pt/protective electrolyte/Pt the bulk ionic conductivity of YSZ and $Bi_{1.75}Sm_{0.25}O_3$ was obtained. These data, along with data for R_3 and Q_3 were used to calculate the Arrhenius plots of the temperature dependence of the oxygen ionic conductivity in YBCO, YBKCO and BPSCCO. These plots are presented in fig. 3. The conductivity activation enthalpies are 1.23 eV

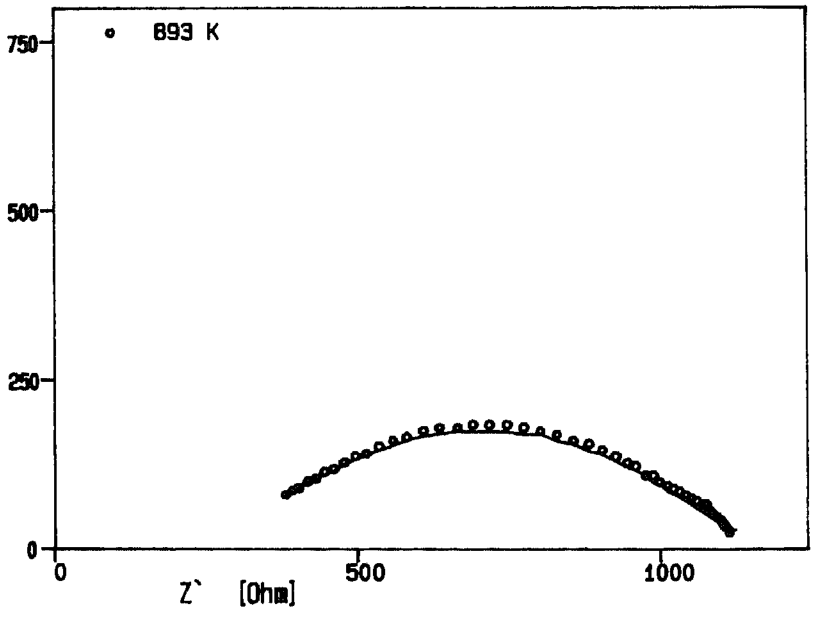

Fig. 1. Impedance spectrum of cell (III) at 893 K. (o) measured, (—) calculated.

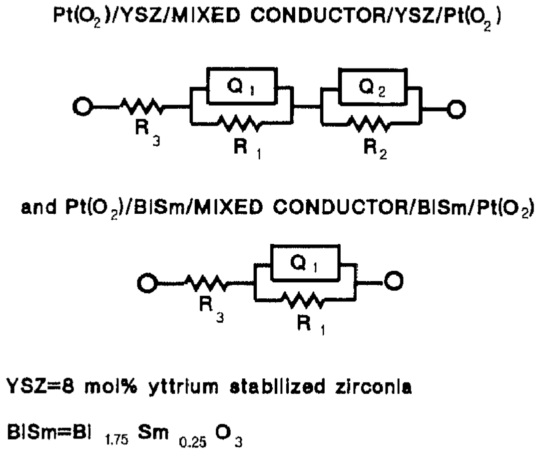

Fig. 2. Equivalent circuits for the solid state electrochemical cells.

(YBCO), 0.94 eV (YBKCO), and 0.87 eV (BPSCCO). These conductivity data have not been corrected for sample porosities. Conductivities at theoretical density can be calculated using the relation between conductivity and porosity [6]

$$\sigma=\sigma_0\,(1-P)^x\,,$$

where σ represents the measured conductivity, σ_0 the conductivity at theoretical density, P the porosity, and x a number which ranges between 1.5 and 2. Taking the correction into account it is apparent that $\sigma(\text{YBKCO})>\sigma(\text{YBCO})$ in line with the introduction of extra oxygen ion vacancies into the lattice to compensate for the effective negative charge of the K'_{Ba} ions. The total electrical conductivity of YBCO is documented very well in the literature. Combined with the present data we obtain for the ionic transference number t_i values varying from 1.15×10^{-6} at 680 K to 2.4×10^{-7} at 980 K. At 777 K the ionic conductivity of YBCO in O_2 ambient has the value 2.13×10^{-4} S cm^{-3}. The oxygen ion vacancy concentration is 1.7×10^{21} cm^{-1} (O_2) [5]. For the mobility μ of the oxygen ion vacancies we obtain at this temperature 3.92×10^{-7} cm^2/Vs. With the Einstein relation, $\mu/D=2q/kT$, we then obtain for the oxygen ion vacancy diffusion coefficient the value 1.31×10^{-8} cm^2/s. This value is concordant with the value of the chemical diffusion coefficient at this temperature [7].

The impedance spectra of the cells (V) and (VI) have been analyzed to obtain oxygen ionic resistivities in Ag. The Arrhenius plots of the temperature

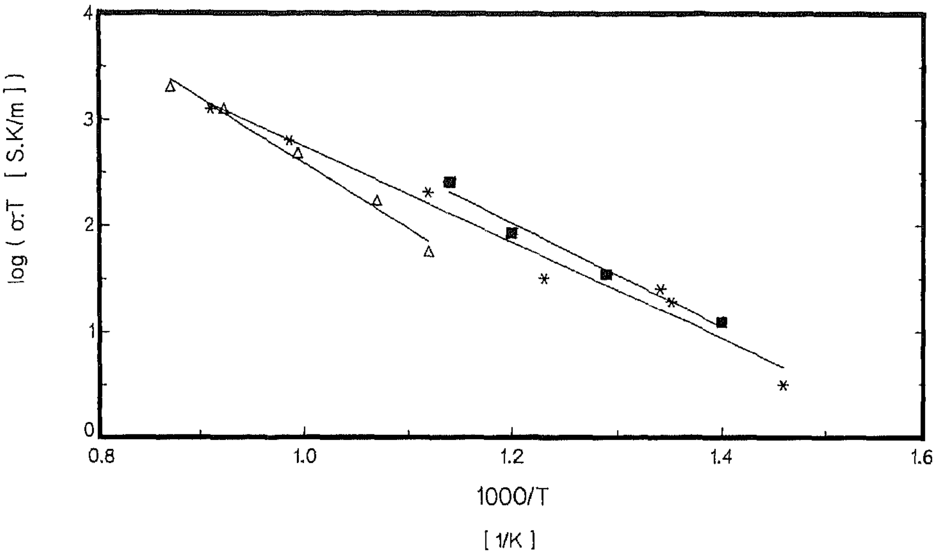

Fig. 3. Arrhenius plots of the temperature dependence of the ionic conductivity in YBCO (△), YBKCO (*), and BPSCCO (■).

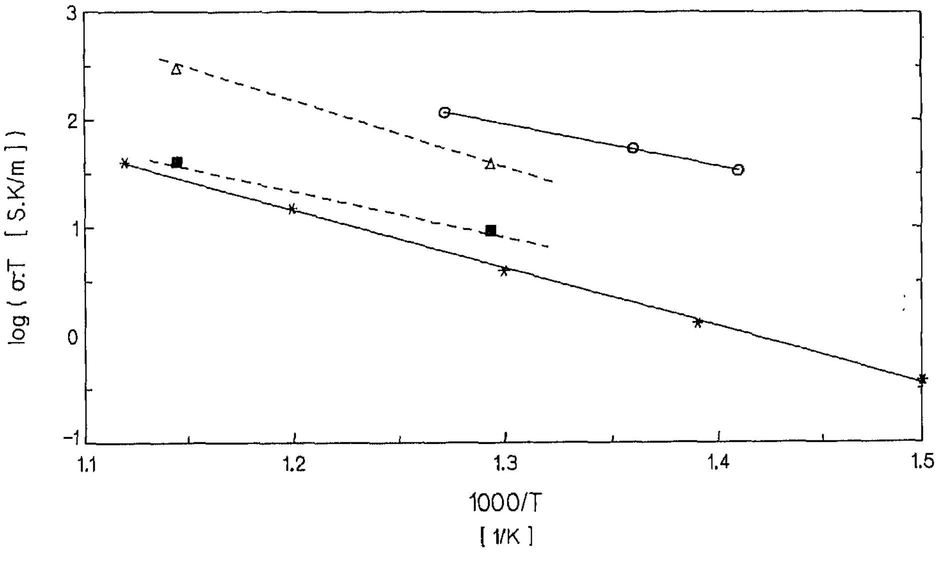

Fig. 4. Arrhenius plots of the temperature dependence of the oxygen ionic conductivity of Ag. Cell (V) (■, △), cell (VI), (o). Bulk ionic conductivity (△, o). Bulk and grainboundary conductivity (■). Calculated from reported oxygen flux data [6] (*).

dependence of the conductivity are given in fig. 4. The results reveal that the bulk oxygen conductivity exceeds the conductivity as calculated from oxygen flux data [8] by a factor of about ten. At low frequencies the impedance spectra of cell (V) revealed a grain boundary polarization effect $R_{gb}C_{gb}p$. Conductivities as calculated from $(R_{bulk}+R_{gb})^{-1}$ are concordant with those calculated from the flux data. It is not unrealistic to assume that flux data have not been corrected for grainboundary effects. The experimental results as obtained with cells (V) and (VI), therefore, indicate that the present solid state electrochemical technique to determine ionic conductivities in HT_cS materials leads to reliable conductivity values and hence diffusion constants.

Acknowledgement

One of the authors (D.J.V.) is indebted to the Netherlands Organization of Applied Scientific Research for financial support.

References

[1] H.I. Yoo, J. Mat. Res. 4 (1989) 23.
[2] D.J. Vischjager, P.J. van der Put, J. Schram and J. Schoonman, Solid State Ionics 27 (1988) 199.
[3] D.J. Vischjager, J. Schram, A. Mackor and J. Schoonman, Silic. Ind. 54 (1989) 153.
[4] D.J. Vischjager, J. Schram, A. Mackor and J. Schoonman, in: Science and technology of thin film superconductors, eds. R.D. McConnell and S.A. Wolf (Plenum Press, New York, London, 1989) p. 441.
[5] A.A. van Zomeren, Internal report 29/6/1989, Delft University of Technology.
[6] C.E. Baumgartner, R.H. Arendt, C.D. Jacovangelo and B.R. Karas, J. Electrochem. Soc. 131 (1984) 2217.
[7] X. Turrillas, J.A. Kilner, I. Kontoulis and B.C.H. Steele, J. Less-Common Met. 151 (1989) 229.
[8] H.H. Mobius, 37th Meeting of ISE (Vilnius, USSR, 1986), Abstract Vol. I, p. 136.