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Oxygen ionic and electronic transport in apatite-type $La_{10-x}(Si,Al)_6O_{26\pm\delta}$

A.L. Shaula[a], V.V. Kharton[a,b,*], F.M.B. Marques[a]

[a] *Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal*
[b] *Institute of Physicochemical Problems, Belarus State University, 14 Leningradskaya Str., 220050 Minsk, Belarus*

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Abstract

The main factor governing the oxygen ionic conductivity in apatite-type $La_{10-x}Si_{6-y}Al_yO_{27-3x/2-y/2}$ ($x = 0-0.33$; $y = 0.5-1.5$) is the concentration of mobile interstitials determined by the total oxygen content. The ion transference numbers, measured by modified faradaic efficiency technique, vary in the range 0.9949–0.9997 in air and increase on reducing oxygen partial pressure due to decreasing p-type electronic conduction. The activation energies for ionic and hole transport are (56–67) ± 3 kJ/mol and (57–100) ± 8 kJ/mol, respectively. Increasing oxygen content leads to higher hole conduction in oxidizing atmospheres and promotes minor oxygen losses from the lattice when the oxygen pressure decreases, although the overall level of ionic conductivity is almost constant in the $p(O_2)$ range from 50 kPa down to 10^{-16} Pa. Under reducing conditions at temperatures above 1100 K, silicon oxide volatilization from the surface layers of apatite ceramics results in a moderate decrease of the conductivity with time. This suggests that the operation of electrochemical cells with silicate-based solid electrolytes should be limited to the intermediate-temperature range, such as 800–1000 K, where the ionic transport in most-conductive apatite phases containing 26.50–26.75 oxygen atoms per unit formula is higher than that in stabilized zirconia. The average thermal expansion coefficients of apatite ceramics, calculated from dilatometric data in air, are $(8.7\text{–}10.8) \times 10^{-6}\,K^{-1}$ at 300–1300 K.

Keywords: Lanthanum silicate; Apatite; Solid oxide electrolyte; Oxygen ionic conductivity; Electronic transport; Faradaic efficiency; Ion transference number; Thermal expansion; Seebeck coefficient

1. Introduction

Oxygen ion-conducting solid electrolytes are key materials for numerous high-temperature electrochemical applications, such as solid oxide fuel cells (SOFCs), gas electrolyzers, oxygen sensors, and electrocatalytic reactors for natural gas conversion [1–3]. These electrochemical technologies provide important advantages with respect to conventional industrial processes. In particular, the use of SOFCs for electric power generation is characterized by a high energy-conversion efficiency, environmental safety and fuel flexibility including the prospects of direct operation with natural gas. Practical application of SOFCs is, however, still limited due to high costs of the component materials and processing. The SOFC-based systems are expected to become commercially feasible when their costs decrease several times, down to approximately 0.7 US$/W [2,3]. Developments of novel oxygen ion-conducting materials, in particular solid electrolytes, are therefore of vital importance in this field.

Recently, a substantial level of oxygen ionic conductivity has been reported for phases derived from apatite-type silicates and germanates with general formula $A_{10-x}(MO_4)_6O_{2\pm\delta}$ ($M =$ Si, Ge), where A are

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[*] Corresponding author. Present address: Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal. Fax: +351 234 425300.
E-mail address: kharton@cv.ua.pt (V.V. Kharton).

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rare- and alkaline-earth cations [4–17]. The apatite lattice tolerance with respect to *A*-site deficiency and to extensive aliovalent doping provides a possibility for further optimization of transport properties of these solid electrolytes. The ionic conduction in $Re_{10-x}Si_6O_{26+\delta}$ ($Re = $ La–Yb; $x = 0-0.67$) increases with increasing radius of Re^{3+} cations, whilst the activation energy decreases; maximum conductivity is characteristic of the La-containing silicates [4,5,7,16]. Similar correlation is well known for perovskite- and K_2NiF_4-type oxides [18]. As for the *A*-site cation radii, the larger size of Ge^{4+} with respect to Si^{4+} results in a higher conductivity for Ge-based apatites compared to analogous silicates, although the activation energies of the former compounds are typically higher [6,15]. However, the Ge-containing materials suffer from Ge volatility and possible transformation into La_2GeO_5 at high temperatures, necessary to sinter dense ceramics [13,15].

The apatite lattice consists of a network of isolated MO_4 tetrahedra creating cavities occupied by *A*-site cations; additional oxygen sites surrounded by the *A*-site ions form channels running through the structure along the *c*-axis. The conductivity data on apatite single crystals, and the results of atomistic modelling, structural refinement and Mössbauer spectroscopy ([7,11–14] and references therein) clearly showed that interstitial migration along these channels has a key contribution to the overall level of ionic transport. Particular consequences include anisotropy of oxygen ion diffusivity, which is essentially higher in the direction parallel to the c-axis, and a decrease of ionic conductivity on decreasing oxygen content, especially below 26 oxygen atoms per apatite unit formula [8,9,12,13,16,17]. The maximum ionic conduction might therefore be expected for $La_{10}Si_6O_{27}$. At the same time, the existence of this phase under equilibrium conditions at SOFC operation temperatures is still questionable [5,8-10]. Although no phase impurities are often indicated in $Re_{10}M_6O_{27}$ ceramics by X-ray diffraction (XRD) analysis [6,9], grain-boundary studies, using electron microscopy, are necessary to confirm the existence of apatites with high oxygen excess as equilibrium phases and the absence of phase segregation. Another important factor affecting ionic transport in the apatite lattice relates to the *A*-site vacancies, particularly in positions enveloping oxygen channels. The *A*-site deficiency influences the SiO_4 tetrahedra relaxation and may cause displacement of the anions from channels into new interstitial sites, thus creating vacancies at fixed oxygen content [10,11,14,16]. For instance, an enhancement of the ionic transport is obtained in the $La_{9.33+x/3}Si_{6-x}Al_xO_{26}$ series, where Al doping is compensated by *A*-site vacancies without oxygen content variations, with maximum conductivity for $x = 1.5$ [10]. The information on electronic conduction in apatite-type silicates is scarce.

This work is focused on the study of $La_{10-x}Si_{6-y}Al_yO_{27-3x/2-y/2}$ ($x = 0-0.33$; $y = 0.5-1.5$) solid electrolytes, with particular emphasis on the properties most relevant for practical applications, namely the partial ionic and electronic conductivities, transference numbers, thermal expansion and stability at low oxygen partial pressures.

2. Experimental

Dense ceramic samples of $La_{10-x}Si_{6-y}Al_yO_{27-3x/2-y/2}$ ($x = 0$, 0.17 and 0.33; $y = 0.5$, 1.0 and 1.5) were prepared by the standard solid-state technique from high-purity La_2O_3, SiO_2 and $Al(NO_3)_3 \cdot 9H_2O$. Before weighting, lanthanum oxide and silica were annealed in air at 1473 and 873 K, respectively. The stoichiometric mixtures were calcined in air at 1023 K for 2 h, ball-milled, and reacted at 1273–1473 K in air. Then the powders were ball-milled again and uniaxially pressed into disks of various thickness at 120–250 MPa. Gas-tight ceramics were sintered at 1923–1973 K during 10 h in air. In all cases, the density of materials was higher than 91% of their theoretical density calculated from XRD data (Table 1).

The XRD patterns were collected at room temperature using a Rigaku D/MAX-B diffractometer (Cu$K\alpha$, $2\Theta = 10-100°$, step 0.02°, 1 s/step); the structural parameters were refined employing the Fullprof program [19]. A Linseis L70 dilatometer (heating rate of 5 K/min) was used to study thermal expansion in air. Microstructure was examined using a Hitachi S-4100 scanning electron microscope (SEM) with a Rontec UHV Detection system for the energy dispersive spectroscopy (EDS). The temperature dependencies of the total conductivity (σ) in flowing air, argon and $10\%H_2$–$90\%N_2$ mixture were measured by AC impedance spectroscopy (HP4284A precision LCR meter, 20 Hz–1 MHz); the oxygen partial pressure in the measuring cell was determined using an yttria-stabilized zirconia (YSZ) oxygen sensor. The values of the activation energy (E_a) were calculated by the standard Arrhenius equation

$$\sigma = \frac{A_0}{T}\exp\left[-\frac{E_a}{RT}\right], \tag{1}$$

where A_0 is the pre-exponential factor. The isothermal measurements of the total conductivity and Seebeck coefficient at 973–1223 K were carried out in the oxygen partial pressure range 1×10^{-16} to 5×10^4 Pa as described elsewhere [20,21]. The oxygen ion transference numbers were determined by the modified faradaic efficiency (FE) technique, taking electrode polarization into account [22]. In combination with the use of electrodes having a relatively high polarization resistance, this method enables to significantly improve the