

Oxygen Ionic Transport in Brownmillerite-Type $\text{Ca}_2\text{Fe}_2\text{O}_{5\pm\delta}$ and Calcium Ferrite-Based Composites

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Abstract. *The present work was centered on the studies of oxygen permeability, mixed conductivity, dilatometric behavior, crystal structure and microstructure of $\text{Ca}_2\text{Fe}_2\text{O}_{5\pm\delta}$ and $\text{Ca}_2(\text{Fe},\text{M})_2\text{O}_{5\pm\delta}$ ($\text{M} = \text{Co}, \text{Mn}$) solid solutions, and dual-phase $\text{Ca}_2\text{Fe}_2\text{O}_5 - \text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ composites. The anisotropic oxygen-ion diffusion in calcium ferrite lattice was simulated using molecular dynamics and atomistic modeling techniques. The computer simulations results were analyzed in light of the experimental data on ionic conduction and thermodynamic stability.*

Key words: oxide-ion diffusion, computer simulations, brownmillerite, oxygen permeation, dimensional stability.

I. INTRODUCTION

Ferrite-based materials with mixed oxygen ionic and electronic conductivity receive a considerable attention for high-temperature electrochemical applications, such as ceramic membranes for oxygen separation and partial oxidation of hydrocarbons, electrodes of solid oxide fuel cells, and sensors. At the same time, perovskite-type ferrites doped with large amounts of alkaline-earth cations exhibit relatively high reactivity with carbon dioxide and sulfur-containing gaseous species, especially in the case of Ba^{2+} and Sr^{2+} , and also high thermal and chemically-induced expansion. This reactivity can be moderated by decreasing A-site cations radius (e.g. by replacing Sr^{2+} with Ca^{2+}). In order to suppress lattice expansivity, the oxygen nonstoichiometry variations with temperature and oxygen partial pressure should be minimized. The present work was centered on the studies of redox and transport properties of undoped $\text{Ca}_2\text{Fe}_2\text{O}_{5\pm\delta}$ brownmillerite and two its derivatives, $\text{Ca}_2\text{Fe}_{1.6}\text{M}_{0.4}\text{O}_{5\pm\delta}$ ($\text{M} = \text{Co}, \text{Mn}$), where the content of the transition metal dopants is close to the solid solution formation limits in air.

II. EXPERIMENTAL

Single-phase, dense ceramics of $\text{Ca}_2\text{Fe}_{2-x}\text{M}_x\text{O}_{5\pm\delta}$ ($\text{M} = \text{Co}, \text{Mn}$; $x = 0-0.4$), were synthesized via glycine-nitrate route and sintered in air at 1420-1550 K. Dense membranes made of dual-phase $\text{Ca}_2\text{Fe}_2\text{O}_5 - \text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ composites, containing approximately 40 vol.% of fluorite-type $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO) solid electrolyte, were made via mixing of submicron powders, ball-milling and sintering at 1420-1570 K. Characterization of the ceramic materials

included XRD, SEM/EDS, inductively-coupled plasma spectroscopic analysis, controlled-atmosphere dilatometry, differential thermal and thermogravimetric analyses, and measurements of the total conductivity (4-probe DC), Seebeck coefficient and steady-state oxygen permeation fluxes as function of temperature and oxygen partial pressure, $p(\text{O}_2)$. The oxidation states and coordination of iron cations were studied by the transmission Mössbauer spectroscopy analysis of powdered samples, equilibrated in air or annealed in various atmospheres and then quenched. The approximate phase stability limits under reducing conditions were derived combining XRD analysis with the data on electrical properties and oxygen content vs. $p(\text{O}_2)$.

The computer simulations employing GULP and DL_POLY software were carried out as described elsewhere [1, 2]. These calculations are based on the Born model for ionic solids; the charge of ions is considered equal to their formal oxidation state. The interactions between the ions are formulated in terms of long-range coulombic forces and two types of short-range interactions, namely the Pauli repulsion and van der Waals dispersion; the short-range forces are modeled using a standard Buckingham potential.

III. RESULTS & DISCUSSION

The oxygen partial pressure dependencies of the total conductivity and Seebeck coefficient of $\text{Ca}_2\text{Fe}_2\text{O}_{5\pm\delta}$ were found typical for perovskite-related ferrites, with a conductivity minimum in the oxygen partial pressure range 10^{-15} - 10^{-10} atm and a hysteresis in the intermediate $p(\text{O}_2)$ range. XRD showed, however, that redox behavior of $\text{Ca}_2\text{Fe}_2\text{O}_{5\pm\delta}$ under moderately reducing conditions is more complex with respect to its perovskite-type analogues. Whilst $\text{Ca}_2\text{Fe}_2\text{O}_{5\pm\delta}$ is single-phase in oxidizing atmospheres, reducing $p(\text{O}_2)$ below 10^{-8} - 10^{-6} atm leads to progressive segregation of CaO traces, without CaFe_2O_4 or iron oxides. This behavior suggests a change in the dominant defect formation mechanism. In agreement with experimental results and computer simulations using the atomistic modeling method, the redox processes in oxidizing atmospheres can be described by oxygen incorporation, hole generation and iron disproportionation reactions. Under reducing conditions, calcium vacancy formation in the brownmillerite lattice starts to contribute to the charge compensation of increasing oxygen deficiency. Within the phase stability domain, the oxygen nonstoichiometry is relatively small, but is reproducible and statistically significant, varying in the range of 0-0.08 atoms per formula unit. These variations can be successfully described by two defect models, accounting for the different redox mechanisms in oxidizing and reducing environments. The calculated enthalpies for oxygen intercalation are -68 ± 8 and -307 ± 2 kJ/mol, respectively. The relatively minor

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changes in the oxygen deficiency in comparison to the perovskite-type ferrites result in a superior dimensional stability of $\text{Ca}_2\text{Fe}_2\text{O}_{5\pm\delta}$ ceramics, as confirmed by high-temperature XRD and controlled-atmosphere dilatometric analyses.

The substitution of cobalt for iron in $\text{Ca}_2\text{Fe}_2\text{O}_{5\pm\delta}$ was found to increase the total conductivity, predominantly p-type electronic in oxidizing atmospheres, and to substantially promote reductive decomposition. A similar effect on the phase stability is observed due to Mn doping, which however decreases electronic transport. The Mössbauer spectroscopy demonstrated a statistical distribution of cobalt and manganese cations between the tetrahedrally and octahedrally coordinated iron sites in the $\text{Ca}_2\text{Fe}_2\text{O}_{5\pm\delta}$ lattice. The ionic conductivity of $\text{Ca}_2\text{Fe}_2\text{O}_{5\pm\delta}$ ceramics calculated from the oxygen permeability data is considerably higher than that in other non-perovskite ferrite phases, such as $\text{Sr}_4\text{Fe}_6\text{O}_{13\pm\delta}$ or $\text{CaFe}_2\text{O}_{4\pm\delta}$, but is lower compared to the disordered perovskite phases such as $\text{Sr}(\text{Fe},\text{Al})\text{O}_{3-\delta}$ [3].

The low oxygen nonstoichiometry variations under oxidizing and moderately reducing conditions, associated with energetically unfavorable oxygen intercalation, and the resultant low chemical expansion/contraction make it possible to consider $\text{Ca}_2\text{Fe}_2\text{O}_{5\pm\delta}$ as a parent compound for the dense ceramic membranes used for oxy-combustion power plants enabling CO_2 capture, and for high-purity oxygen separation at elevated pressures. These applications require, however, to substantially increase oxygen permeability of calcium ferrite-based ceramics, which is essentially limited by the bulk ion diffusion. Such an increase can be achieved by forming dual-phase oxide composites comprising a solid electrolyte component with high ionic conductivity. In this work, this concept was tested by the example of $\text{Ca}_2\text{Fe}_2\text{O}_5$ – CGO system, where the components are sufficiently stable with respect to cation interdiffusion at elevated temperatures. Testing of $\text{Ca}_2\text{Fe}_2\text{O}_5$ – $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ composites with submicron grain size demonstrated that the ionic transport and oxygen permeability can be considerably increased by adding gadolinia-doped ceria as the second, ion-conducting, phase, whilst the thermal expansion and other functional properties remain almost unchanged. The oxygen permeation fluxes

can be further increased via optimization of the $\text{Ca}_2\text{Fe}_2\text{O}_5$ – CGO volume ratio and via surface modification of the ceramic membranes, as interfacial exchange affects their performance. Furthermore, the permeation through dual-phase composites becomes affected by the electronic transport, thus making it necessary to substitute iron in $\text{Ca}_2\text{Fe}_2\text{O}_5$ by other transition metal cations increasing p-type electronic conductivity, such as cobalt.

The computer simulation studies showed that the defect-formation and ion diffusion processes in $\text{Ca}_2\text{Fe}_2\text{O}_{5\pm\delta}$ lattice are essentially governed by the perovskite-like layers, as for Ruddlesden-Popper type ferrites. These layers, where both equatorial and apical oxygen positions contribute to the anion mobility, are characterized by lower vacancy-formation and migration energies compared to the sheets consisting of iron-oxygen tetrahedra. In the latter case, the defect reactions and oxygen diffusion may be affected by extra factors, such as local distortions and even rotation of the tetrahedra, leading to additional energetic barriers. At the same time, Fe^{2+} states formed in the tetrahedral layers may be involved in defect clustering processes with the oxygen vacancies located in the apical sites of perovskite-type sheets. This behavior increases significance of cooperative migration processes, when vacancy migration is coupled with electron-hole transfer.

ACKNOWLEDGMENT

This work was supported by the FCT, Portugal (projects PTDC/CTM-CER/114561/2009, PTDC/CTM/64357/2006, SFRH/BPD/28913/2006 and POCI/CTM/ 58570/ 2004).

REFERENCES

- [1] E.N. Naumovich, V.V. Kharton, "Atomic-scale insight into the oxygen ionic transport mechanisms in La_2NiO_4 -based materials", *Journal of Molecular Structure: THEOCHEM*, vol. 946, no. 1-3, pp. 57-64, 2010.
- [2] A.A. Markov, M.V. Patrakeev, V.V. Kharton, Y.V. Pivak, I.A. Leonidov and V.L. Kozhevnikov, "Oxygen nonstoichiometry and ionic conductivity of $\text{Sr}_3\text{Fe}_{2-x}\text{Sc}_x\text{O}_{7-\delta}$ ", *Chemistry of Materials*, vol. 19, pp. 3980-3987, 2007.
- [3] A.L. Shaula, Y.V. Pivak, J.C. Waerenborgh, P. Gaczynski, A.A. Yaremchenko, V.V. Kharton, "Ionic conductivity of brownmillerite-type calcium ferrite under oxidizing conditions", *Solid State Ionics*, vol. 177, pp. 2923-2930, 2006.