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Late I - 2418 - Oxygen-Deficient $(Ln,Sr)_2NiO_{4-\delta}$ Nickelates for Oxygen Electrodes of Solid Oxide Fuel and Electrolysis Cells: Anisotropic Thermochemical Expansion and Thermomechanical Constraints

Tuesday, 31 May 2022

18:00 - 20:00

Vancouver Convention Center - West Ballroom B/C/D

Abstract

Perovskite-like and perovskite-related oxides based on variable-valence transition metals may exhibit substantial changes in oxygen content in the course of temperature cycling or under variation of oxygen chemical potential at elevated temperatures. This gives rise to a chemical contribution to the thermal expansion (chemical expansion/contraction or chemical strain) originating mainly from the accompanying changes in the average oxidation state of transition metal cations and, consequently, their ionic radii. Excessive dimensional changes caused by the chemical expansion impose constraints on the applicability of functional oxides at elevated temperatures and under variable redox conditions (due to thermomechanical instability or incompatibility with other materials) and complicate the processing of oxide ceramics at high temperatures. Another unfavorable phenomenon is microcracking caused by a strongly anisotropic expansion of crystal lattice, with effects on the microstructural and mechanical integrity and electrical and electrochemical properties. The present work is a representative study case that focuses on layered Ln_2NiO_4-based ceramic materials for oxygen electrodes of solid oxide fuel/electrolysis cells (SOFC/SOEC).

$Ln_2NiO_{4+\delta}$–based oxides (Ln = La, Pr, Nd) with perovskite-related K_2NiF_4-type structure demonstrate high oxygen diffusivity and surface exchange kinetics in combination with comparatively high electronic conductivity and are considered, therefore, as attractive mixed ionic-electronic conductors for oxygen electrodes of high-temperature SOFC/SOEC [1]. Acceptor-type substitution of Ln^{3+} by Sr^{2+} in $Ln_2NiO_{4+\delta}$ is compensated by comparatively high oxygen deficiency in Sr-rich $Ln_{2-x}Sr_xNiO_{4-\delta}$ phases at elevated temperatures [2,3]. The transition from oxygen excess to oxygen deficiency is expected to be accompanied by a change in the ionic transport mechanism from prevailing interstitial oxygen diffusion in rock-salt layers to oxygen vacancy diffusion in perovskite-type layers.

Ceramic powders of $Ln_{2-x}Sr_xNiO_{4-\delta}$ (Ln = La, Nd, Pr, x = 1.0-1.6) were prepared by the Pechini method with final calcination steps at 1150-1200°C in oxygen. Thermogravimetric studies confirmed that acceptor-type substitution by strontium is compensated by the formation of oxygen vacancies and electron-holes and progressively increases high-temperature oxygen nonstoichiometry (Fig.1A), which reaches as high as δ = 0.36-0.40 for x = 1.6 at 900°C in air. High-temperature XRD studies demonstrated that $Ln_{2-x}Sr_xNiO_{4-\delta}$ nickelates exhibit strongly anisotropic lattice expansion interrelated with oxygen deficiency changes on heating (Fig.1B). Highly anisotropic expansion induces microcracking phenomenon, which, in turn, results in a strong hysteresis in dimensional changes (Fig.1C) and also in variations of electrical conductivity (Fig.1D) on cycling in air for the ceramic samples sintered at 1200-1300°C.

An appropriate approach to minimize or neglect the undesirable effects of anisotropic expansion and microcracking is to preserve the grain size in $Ln_{2-x}Sr_xNiO_{4-\delta}$ ceramics or porous electrodes at ~1 micron or submicron level. In particular, spark plasma sintering with subsequent careful oxidation treatment was adopted to avoid grain growth and to produce mechanically stable ceramics with smooth reversible thermochemical expansion and enhanced electrical properties.

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References:

[1] A.P. Tarutin, J.G. Lyagaeva, D.A. Medvedev, L. Bi, A.A. Yaremchenko, Recent advances in layered $Ln_2NiO_{4+\delta}$ nickelates: fundamentals and prospects of their applications in protonic ceramic fuel and electrolysis cells, Journal of Materials Chemistry A 9 (2021) 154-195. https://doi.org/10.1039/D0TA08132A

[2] E. Kravchenko, D. Khalyavin, K. Zakharchuk, J. Grins, G. Svensson, V. Pankov, A. Yaremchenko, High-temperature characterization of oxygen-deficient K_2NiF_4-type $Nd_{2-x}Sr_xNiO_{4-d}$ (x = 1.0-1.6) for potential SOFC/SOEC applications, Journal of Materials Chemistry A 3 (2015) 23852-23863. https://doi.org/10.1039/C5TA06779K

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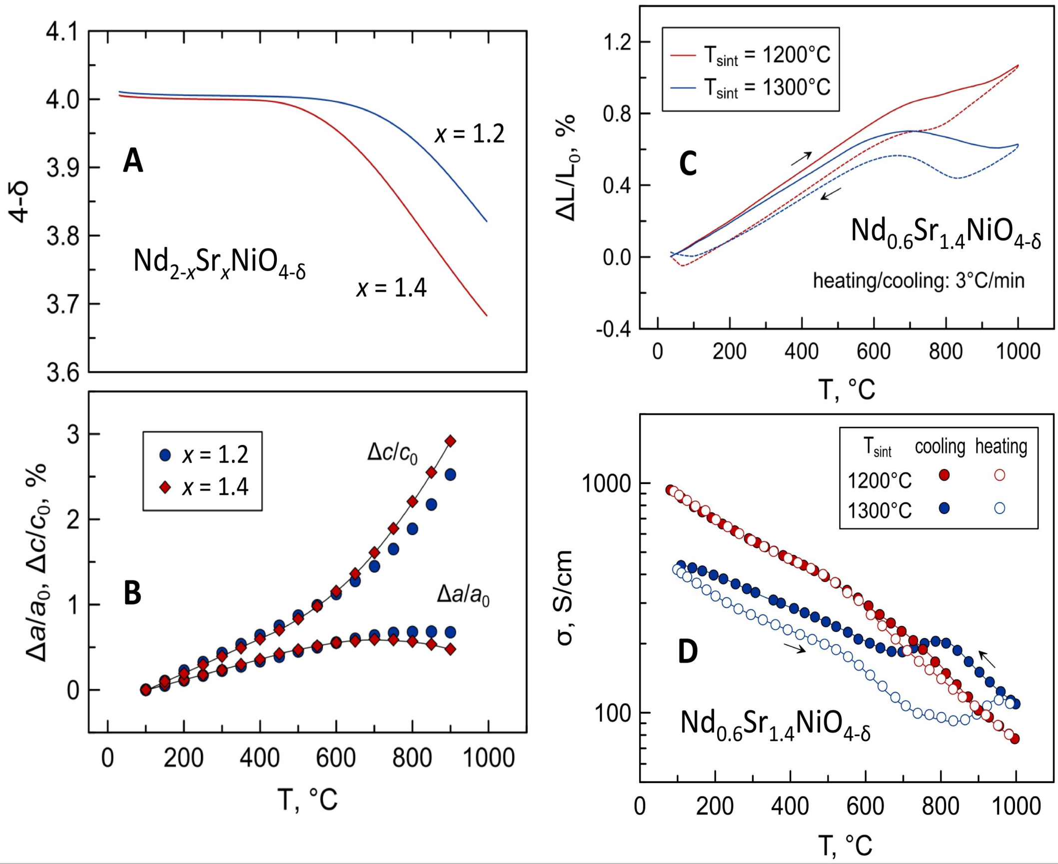
Figure 1. (A) Oxygen nonstoichiometry of $Nd_{2-x}Sr_xNiO_{4-\delta}$ nickelates in air; (B) relative elongation of $Nd_{2-x}Sr_xNiO_{4-\delta}$ tetragonal lattice along the crystallographic *a* and *c* axes on heating in air; (C) dimensional changes and (D) variations in electrical conductivity of $Nd_{0.6}Sr_{1.4}NiO_{4-\delta}$ ceramics (sintered either at 1200 or 1300°C) on thermal cycling in air.



Corresponding Author

Y

Aleksey Yaremchenko
CICECO - Aveiro Institute of Materials, University of Aveiro

Authors

Z

Kiryl Zakharchuk
CICECO - Aveiro Institute of Materials, University of Aveiro

K

Ekaterina Kravchenko
Faculty of Chemistry, Belarusian State University
CICECO - Aveiro Institute of Materials, University of Aveiro

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