Available online at www.sciencedirect.com

ScienceDirect

Physics Procedia 84 (2016) 397 – 406

Physics Procedia

International Conference "Synchrotron and Free electron laser Radiation: generation and application", SFR-2016, 4-8 July 2016, Novosibirsk, Russia

Application of SR methods for the study of nanocomposite materials for Hydrogen Energy

V.A. Sadykov[a,b,]*, S.N. Pavlova[a], Z.S. Vinokurov[a,b], A.N. Shmakov[a,b,c], N.F. Eremeev[a,b], Yu.E. Fedorova[a,b,d], E.P. Yakimchuk[a], V.V. Kriventsov[a,c], V.A. Bolotov[a], Yu.Yu. Tanashev[a], E.M. Sadovskaya[a,b], S.V. Cherepanova[a], K.V. Zolotarev[c]

.

[a]Boreskov Institute of Catalysis SB RAS, Novosibirsk 630090, Russian Federation
[b]Novosibirsk State University, Novosibirsk 630090, Russian Federation
[c]Budker Institute of Nuclear Physics SB RAS, Novosibirsk 630090, Russian Federation
[d]Novosibirsk State Pedagogical University, Novosibirsk 630126, Russian Federation

---

Abstract

This work summarizes results of synchrotron radiation (SR) studies of the real/defect structure of nanocrystalline/nanocomposite oxide materials, which determines their functional properties in hydrogen energy field as catalysts and mixed ionic electronic conductors (cathodes and anodes of solid oxide fuel cells, oxygen separation membranes). For nanocrystalline ceria-zirconia mixed oxide prepared via modified Pechini route using ethanol solution of reagents, a high spatial uniformity of cations distribution between domains along with the oxygen sublattice deficiency revealed by full-profile Rietveld refinement of SR diffraction data provide structure disordering enhancing oxygen mobility. For $PrNi_{0.5}Co_{0.5}O_{3-\delta}$ – $Ce_{0.9}Y_{0.1}O_{2-\delta}$ nanocomposite extensive transfer of Pr cations into fluorite domains generates a new path of fast oxygen diffusion along chains of Pr^{3+} – Pr^{4+} cations as directly proved by analysis of the unit cell relaxation after changing pO_2 in perfect agreement with data obtained by oxygen isotope heteroexchange.

---

* Corresponding author. Tel.: +7-383-326-95-41; fax: +7-383-330-80-56.
E-mail address: sadykov@catalysis.ru

doi:10.1016/j.phpro.2016.11.068

Keywords: SOFC; catalytic membrane reactors; perovskite-fluorite nanocomposites; oxygen mobility; unit cell volume relaxation; synchrotron radiaton; XAFS.

Nomenclature

D_{chem}	chemical diffusion coefficient
D_O	oxygen tracer diffusion coefficient
k_{chem}	chemical exchange constant
k_{ex}	oxygen surface exchange constant
pO_2	oxygen partial pressure

1. Introduction

In the emerging field of Hydrogen Energy, tailor-made design of the active components of sensors, monolithic catalysts for selective oxidation/autothermal reforming of hydrocarbons into syngas at short contact times (Sadykov et al. (2011)), water gas shift reaction (Li et al. (2000)) and preferential oxidation of CO in the hydrogen excess is based upon the concept of the bifunctional reaction mechanism where the oxygen mobility in complex oxide fluorite-like support (doped ceria or ceria-zirconia) plays an important role (Sadykov et al. (2010)). High oxygen mobility and surface reactivity are also required for components of solid oxide fuel cells (SOFC) and solid oxide electrolyzers (Irvine et al. (2016)) including cathodes to avoid limiting by triple-phase boundary (Huang et al. (2012), Sadykov et al. (2015)). Another problem associated with SOFC cathodes is deterioration due to insufficient chemical stability at working temperatures leading to carbonization and interaction with electrolyte (Ormerod (2003), Sadykov et al. (2015)).

Materials with a high ionic and mixed ionic-electronic conductivity have been gaining attention in recent years as functional layers for such electrochemical and catalytic devices. Complex oxide nanocomposites with perovskite-like and fluorite-like structures are known to be good ionic or mixed ionic-electronic conductors (Sadykov et al. (2015), Steele (2000)). In particular, promising materials are perovskites and Ruddlesden-Popper phases with Pr in the A-site (Huang et al. (2012), Sadykov et al. (2013) and (2015)), doped by Pr and/or Y/Gd/Zr CeO_2-based fluorites (Sadykov et al. (2015), Sinev et al. (1996)), and nanocomposites based upon them.

Doping CeO_2 can improve oxygen mobility and surface reactivity. Y/Gd/Zr-doped ceria fluorites show significantly higher oxygen mobility and surface reactivity characteristics if they are co-doped by Pr. This is the result of Pr cations being able to easily change their charge and therefore to vary the oxygen content in close proximity (Borchert et al. (2005), Sinev et al. (1996), Sadykov et al. (2014)). Ordered $Pr^{3+/4+}$ chains can provide rapid charge transfer and fast oxygen anions/vacancies migration. Thus, such fluorites can show high ionic or mixed ionic-electronic conductivity depending on Pr content (Shuk et al (1999)), which makes them promising materials for functional layers of solid oxide fuel cells, catalytic membrane reactors and other electrochemical and catalytic devices. This effect was shown for Pr- (Sinev et al. (1996)), Pr- and Y- (Sadykov et al. (2015)) and Pr- and Zr-doped ceria (Sadykov et al. (2007)).

The other point of interest in Pr- and Y/Gd/Zr-doped ceria fluorites is their nanocomposites with perovskite or Ruddlesden-Popper oxide possessing unique functional characteristics due to developed perovskite – fluorite interface and cation redistribution between phases, the most pronounced for Pr cations. In our previous studies of $PrNi_{0.5}Co_{0.5}O_{3-\delta}$ – $Ce_{0.9}Y_{0.1}O_{2-\delta}$ nanocomposite (Sadykov et al. (2014) and (2015)), the average fluorite phase composition for samples sintered at high temperatures was shown to be around $Ce_{0.65}Pr_{0.25}Y_{0.1}O_{2-\delta}$.

Defect structure of these complex oxide and nanocomposite systems is considered as an important factor in ensuring their high performance. However, traditional X-ray diffraction techniques are known to be rather restricted in elucidation atomic-scale details of the real structure responsible for the transport properties of these systems. This is the reason why synchrotron radiation (SR) studies (XANES, EXAFS, XRD) of the real/defect structure of complex oxide nanocomposites become tremendously important. This work summarizes results of these SR studies including research of such systems as Pr- and/or Y/Zr-doped ceria, Pr nickelates-cobaltites, Pr(III,IV) oxide and nanocomposites based upon them.