

ELECTROPHYSICAL AND X-RAY SPECTRAL INVESTIGATION OF THE DOPED SM-NICKELITES BASED ELECTRODE MATERIALS

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Introduction

Lowering the operating temperature of solid oxide fuel cells (SOFCs) can increase incidence of this technology. In order to lower the operating temperature, reduction of the polarization resistances occurred at electrode/electrolyte interfaces is important. The interfacial resistances are dramatically increased as the operating temperature is reduced, especially the resistance of oxygen reduction reaction. Therefore, selecting a high-performance cathode material and constructing a suitable cathode/electrolyte interface remain major challenges facing the development of reduced temperature SOFCs.

Results of electrophysical investigation new cathode materials based on samarium nickelites for reduced temperature SOFCs will be briefly considered in this report.

Nickel mixed oxides bring an example of rich chemical and physical properties on the basis of the existence of various formal oxidation states of the Ni atoms (Ni^{2+} or Ni^{3+}). These compounds have regained interest since the discovery of high-temperature superconductivity and giant magnetoresistive effects in other perovskite-related systems. Although the nickelates do not display any of these exotic properties, they are, together with cuprates and manganites, one of the rare families of oxides, which show metallic conductivity. It can be used as electrodes in electrochemical devices such as SOFCs, polymer electrolyte membrane fuel cells (PEMFCs) and molten carbonate fuel cells (MCFCs). LaNiO_3 epitaxial film is used as electrodes to fabricate ferroelectric device.

From the structural point of view, the RNiO_3 compounds ($\text{R}=\text{rare earth}$) are orthorhombically distorted perovskites [1]. The forebear of this structural family is the mineral 'perovskite' (CaTiO_3). The ideal cubic structure consists of a 3D array of corner-sharing NiO_6 octahedra, located at the nodes of a simple cubic lattice. At the centre of the unit cell ($(1/2 \ 1/2 \ 1/2)$ position) there is room for the R cation. The R position must be occupied by a cation with the adequate oxidation state (in order to assure the electrical neutrality) and whose size satisfies the condition.

In the case of the RNiO_3 perovskites, the rare earth is too small to satisfy this criterion. Thus, the NiO_6 octahedra, which have been found to remain practically undistorted along the series, are tilted to fill the extra interstitial space. These rotations cause the unit cell to be smaller and more distorted than the ideal cubic cell. Since the magnitude of this distortion is related to the relative distances $d_{\text{Ni-O}}$ and $d_{\text{R-O}}$, it can be discussed in terms of the tolerance factor defined as $t=d_{\text{R-O}}/(1.41d_{\text{Ni-O}})$.

Metallic conductivity was observed in LaNiO_3 . Very recently, insulator-metal transition were discovered in the Sm, Nd and Pr compounds, in which the transition temperature strongly decreased with increasing size of the rare-earth ion.

Nickelates have been prepared under high oxygen pressure (for $\text{R}=\text{Sm, Eu, Gd}$ under 200 bar in an O_2 atmosphere) or high hydrostatic pressure ($\text{R}=\text{Dy, Ho, Y}$) in the presence of KClO_4 .

The crystal structures of nickelates $\text{R}_{n+1}\text{Ni}_n\text{O}_{3n+1-\delta}$ ($n=1-3$) are similar to those of the Ruddlesden-Popper series $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ [2]. The $n=\infty$ member of this series corresponds to the three-dimensional above-mentioned perovskite RNiO_3 . The nickelates commonly possess oxygen atom deficiency, which affects their transport properties. We researched earlier the electronic structure and electrophysical characteristic of pure and doped $\text{La}_{2n+1-x}\text{Ca}_x\text{Ni}_n\text{O}_{3n+1-\delta}$ ($n=1-3$) based materials [3-5].

We have made an attempt to create an electroconductivity Sm-nickelite based ceramic without use of high pressure O_2 . With this purpose the 3-valent nickel increased contents in compounds has been reached by synthesis of heterovalent solid solution $\text{Sm}_{2-x}\text{Ca}_x\text{NiO}_{4-\delta}$.

Experimental

Doped samarium nickelate polycrystalline ceramics specimen was prepared by the conventional solid state synthesis technique. First, the mixed in distilled water powder of Sm_2O_3 , NiO and CaCO_3 was dried and pressed into pellets and calcined in air at 1000 °C for 4 h. After powdering and mixed well, the powder was pressed into pellets and sintered in air at 1250 °C for 5 h.

X-ray powder diffraction (XRD) patterns were collected for phase identification and to assess

phase purity using CuK_α radiation in a DRON-1.5 diffractometer controlled by a computer.

XRD of this specimen showed a orthorhombic single phase with space group Fmm2.

A four-probe ac (33.3 Hz) technique was employed to measure the electrical resistivities of all of the samples over the temperature range 300–1200 K. We preferred an ac technique over a dc technique because (a) it is faster, (b) it gives a better signal-to-noise ratio and (c) it automatically cancels thermal emfs. Selective nanovoltmeter (model 237), and X-Y recorder (model PDP-4) were used. A measuring current of 1–10 mA from voice-frequency generator G3-33 was used. The absolute accuracy of the resistivity is about 10%.

In order to perform X-ray absorption spectroscopy (XAS) measurements, few mg of powder sample is mixed with diffusion pump oil and spreaded on ashless filter paper. In this way, a thin and homogeneous sample-absorber optimized for transmission measurements is obtained. We performed XAS measurements around Ni K edge ($E=8333$ eV [6]). Absorption spectra were measured in transmission mode using a copper X-ray tube brake radiation with 30 kV anode voltage of the X-ray diffractometer (DRON-1.5) [7]. The crystals-monochromator (the flat quartz crystal with $2d=0.236013$ nm) were installed instead of specimen for XRD-analysis on a goniometer. The sample-absorber is located in exchange of K_β -radiation a cutting filter. The registration of reflected by crystal-monochromator with a known interplanar distance and past through an absorber X-ray intensity, was carried by the scintillator counter during standard $\theta/2\theta$ rotation of a table with crystal- monochromator and counter. The scanning rate has been $0.25\text{deg}_{2\theta}\cdot\text{min}^{-1}$.

The position of the absorption K-edge for pure Ni and its compounds in which the metal had various valence states was measured. On transition

from Ni to NiO and then to lanthanum nickelate LaNiO_3 (in which nickel mainly trivalent) position to K-edge displaced in the short-wave party on 7.0 eV and then on 4.2 eV, accordingly. With use of similar calibration curve was investigated Ni-atoms valent state in examined doped Sm-nickelites.

References

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