Oxygen permeability of $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ ceramics: effect of synthesis method

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Abstract

Oxygen ionic transport in dense $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ membranes, prepared by the standard ceramic synthesis technique and via glycine-nitrate process (GNP), was studied using measurements of the total conductivity, oxygen permeation and faradaic efficiency (FE). At 1223 K oxygen transfer through $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ ceramics is mainly determined by the bulk ambipolar conductivity, while decreasing temperature leads to a greater role of the surface exchange rate. In spite of moderate difference in the ceramic microstructures, the surface exchange limitations are considerably higher for the membranes prepared by the standard ceramic route compared to GNP-synthesized material. Thermal expansion and partial ionic and electronic conductivities were found essentially independent of the synthesis method. The level of oxygen ionic conduction in $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$, characterized by the activation energy of about 150 kJ/mol and ion transference numbers in the range 1×10^{-3} – 5×10^{-2} at 973–1223 K, is higher than that in $\text{La}(\text{Ga},\text{Ni})\text{O}_{3-\delta}$ perovskites and comparable to La_2NiO_4 -based phases.

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1. Introduction

Mixed-conducting ceramic membranes are of considerable interest for applications in electrocatalytic reactors for oxygen separation and conversion of light hydrocarbons to value-added products, particularly the conversion of natural to synthesis gas [1–7]. Conventional technologies for methane conversion are based on steam reforming and/or partial oxidation processes. Steam reforming is energy-intensive due to highly endothermic nature of the reaction, whereas the most significant cost associated

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with partial oxidation is that of an oxygen plant. The membrane technologies may have substantial economic benefits due to the possibility to combine oxygen separation from air and partial oxidation in a single reactor [1–5]. However, mixed-conducting ceramics known at present possess various specific disadvantages, limiting their applicability for the membrane reactors. In particular, perovskite-like solid solutions based on $(\text{Sr},\text{La})(\text{Fe},\text{Co})\text{O}_{3-\delta}$ exhibit attractively high oxygen permeation fluxes, but are thermodynamically and/or dimensionally unstable under large oxygen chemical potential gradients [3–7]. To some extent, the stability of $(\text{Sr},\text{La})(\text{Fe},\text{Co})\text{O}_{3-\delta}$ can be improved by partial substitution of the B-site cations with ions having a higher oxidation state, such as Cr [3,5,6] or Ti [5,8]. This type of doping leads, however, to a decrease in the ionic conductivity and oxygen permeability (OP) [8,9].

One alternative approach in the development of membrane materials refers to incorporation of variable-valence cations in the lattice of solid electrolytes in order to increase their electronic conductivity [1]. While solid solubility of most such dopants in the fluorite phases, e.g. stabilized ZrO_2 and CeO_2 , is low, large amounts of transition metal cations can be dissolved in the perovskite structure of $\text{La}(\text{Sr})\text{Ga}(\text{Mg})\text{O}_{3-\delta}$ (LSGM), resulting in a high mixed conductivity [4,10–12]. A promising combination of properties, including remarkable oxygen permeability and low thermal expansion, was previously found in the perovskite system $\text{La}(\text{Ga},\text{Ni})\text{O}_{3-\delta}$ [11,12]. As the ionic transport in LaGaO_3 -based phases occurs via a vacancy mechanism, increasing nickel content in $\text{La}(\text{Ga},\text{Ni})\text{O}_{3-\delta}$ increases ionic conductivity, but may be undesirable from the stability point of view. Continuing this research, the present paper is focused on the study of $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ ceramics where the concentration of nickel is chosen minimum, necessary to provide sufficient electronic conduction, and magnesium is added as a passive acceptor-type dopant increasing oxygen deficiency.

Particular emphasis in the present work is given to the assessment of relationships between the synthesis method, microstructure and oxygen transport properties. The preparation procedure may significantly affect both ionic conductivity and oxygen surface exchange of ceramic materials [13–17], though unambiguous interpretation of observed phenomena is often difficult due to the complex nature of transport processes at the grain boundaries and on the surface. The oxygen ionic conductivity of single-phase materials, prepared by a similar method with monotonous variation of the processing conditions, typically increases with increasing grain size due to lower grain-boundary resistance [13,17]. At the same time, LaCoO_3 -ceramics prepared using different powder synthesis techniques, namely a cellulose-precursor route and the combustion method, were shown to have similar size of the grains, but drastically different level of the ionic transport [15,16]. As the development of membrane materials requires knowledge, mainly empirical, on the role of processing route, the present work compares properties of $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ samples synthesized by the standard ceramic technique and via the glycine-nitrate process (GNP). The latter, a self-combustion method using glycine as fuel and nitrates of the metal components as oxidant, is well known as especially appropriate for multi-component perovskite systems [18,19].

2. Experimental

The standard ceramic synthesis procedure of $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ powder included mixing of the stoichiometric amounts of high-purity La_2O_3 , Ga_2O_3 , $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with subsequent thermal decomposition of nitrates. Before weighing, lanthanum and gallium oxides were annealed in air at 1270 K for 3–4 h. The mixtures were reacted at 1420–1620 K during 50 h

with multiple intermediate grinding steps. After X-ray diffraction (XRD) analysis confirmed formation of a single perovskite-type phase, the powder was ball-milled; ceramic samples were pressed at 250–350 MPa and then sintered in air at 1798 ± 5 K for 5 h. This processing route is referred to as Method 1.

In the course of GNP (Method 2), glycine was added in an aqueous nitrate solution, containing metal cations in the stoichiometric proportion (molar glycine/nitrate ratio of 1.5). After drying and firing, the resultant powder having a foamed structure was ball-milled and then pressed. The green compacts were sintered in air at 1723 ± 10 K for 5 h. XRD showed that the starting powder prepared by GNP contained several oxide phases; the ceramics was single-phase due to completing solid-state reaction during the sintering.

The sintered ceramic samples were polished with diamond pastes, annealed in air at 1270–1470 K for several hours, and slowly furnace-cooled in order to obtain equilibrium oxygen content. The density of ceramic materials was 95–98% of their theoretical density calculated from XRD results (Table 1). The cation composition was verified by ion-coupled plasma (ICP) spectroscopic analysis. The characterization of ceramic materials included also scanning electron microscopy combined with energy dispersive spectroscopy (SEM/EDS), dilatometry, infra-red (IR) absorption spectroscopy, and the measurements of total conductivity by 4-probe DC technique. The experimental procedures and equipment used for the characterization were reported elsewhere ([8,11,12,14–17] and references cited). Structural parameters were refined from XRD data using the Fullprof program [20]. Thermal expansion was measured using an alumina Linseis dilatometer with a constant heating rate of 3 K/min, in air. The oxygen ionic transport was studied using the measurements of steady-state oxygen permeability (OP) and faradaic efficiency (FE), as described elsewhere [12,14,21]. All data on the oxygen permeability presented in this paper correspond to the membrane feed-side oxygen partial pressure (p_2) equal to 21 kPa (atmospheric air); the faradaic efficiency results were obtained under zero oxygen chemical potential gradient in air [21]. The thickness of the ceramic membranes (d) varied from 0.60 to 2.50 mm.

Table 1
Properties of $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ ceramics

Preparation	Sintering temperature (K)	Unit cell parameters		$\rho_{\text{exp}}/\rho_{\text{theor}}$ (%)	Thermal expansion coefficients	
		a (nm)	α^0		T (K)	$\bar{\alpha} \times 10^6$ (K^{-1})
Method 1	1798	0.5466	60.66	97.9	373–773 773–1273	11.58 ± 0.01 16.99 ± 0.02
Method 2	1723	0.5479	60.49	95.0	373–850 850–1273	11.85 ± 0.02 18.4 ± 0.3
Preparation	Total conductivity (500–1130 K)		Oxygen ionic conductivity (973–1223 K)			
	E_a (kJ/mol)	$\ln(A_0)$ (S K/cm)	E_a (kJ/mol)	$\ln(A_0)$ (S K/cm)		
Method 1	25.4 ± 0.6	9.9 ± 0.1	155 ± 7	20 ± 1		
Method 2	28.3 ± 0.5	10.5 ± 0.1	150 ± 20	19 ± 2		

a and α are the parameters of rhombohedrally-distorted perovskite lattice (space group $R\bar{3}c$). $\rho_{\text{exp}}/\rho_{\text{theor}}$ is the ratio of experimental and theoretical densities. E_a and A_0 are the activation energy and pre-exponential factor of the standard Arrhenius model for conductivity.

3. Results and discussion

SEM/EDS studies revealed no significant difference in the microstructures of $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ ceramics prepared by the different techniques, except for the average grain size. As expected, using of GNP resulted in smaller grains (5–8 μm), whereas in the case of Method 1 the grain size was up to 15–18 μm . One representative example of SEM micrographs is given in Fig. 1. No traces of a liquid phase formation or phase segregation at the boundaries were detected, in agreement with XRD data; the cation distribution along grains and grain boundaries was found uniform for both materials, within the limits of experimental uncertainty of EDS method. The IR spectra of powders obtained by grinding of sintered ceramics were also similar. Therefore, one may suppose that using of the different synthesis techniques did not lead to significant compositional variations, detectable by the standard analytical techniques, which may affect bulk properties of the materials. This well corresponds to the data on total and ionic conductivities and thermal expansion.

On the other hand, $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ ceramics prepared by Method 2 exhibit a larger unit cell volume and smaller rhombohedral angle α (Table 1). Moreover, as discussed below, the oxygen surface exchange rate of this material is considerably higher than that of membranes prepared by Method 1. It seems quite unlikely that such phenomena might result simply from the different concentrations of grain boundaries per unit volume, which are rather comparable (Fig. 1). Exact reasons for this behavior are still unclear; one possible hypothesis may refer to a greater concentration of extended defects in the material made from the nanosized non-single-phase powder, obtained via GNP. Indeed, the transmission electron microscopic (TEM) inspection showed that the size of GNP-synthesized powder particles is in the range 10–100 nm, in agreement with literature [19]. The particle size of the powder prepared by Method 1 is of micron-scale, available for evaluation by SEM. For the material synthesized by Method 2, the ceramic grains are hence formed from a substantially large number of nanosized particles, sintered and reacted in the course of firing. The resultant high concentration of extended defects may lead to local inhomogeneities in the point defect distribution in this material, affecting both lattice parameters and surface properties.

The studies of thermal expansion and total conductivity (Figs. 2 and 3) showed that these properties are essentially independent of the powder synthesis route. The difference in the dilatometric curves and

Fig. 1. SEM micrographs of $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ ceramics prepared by the different methods.

Fig. 2. Dilatometric curves of $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ ceramics in air.

conductivity values of the ceramics, made using Methods 1 and 2, is minor, comparable to the experimental errors. Such a difference may appear, for example, due to stagnated oxygen exchange with the gas phase in the course of heating/cooling during the measurements, which may prevent re-equilibration of the oxygen stoichiometry. As shown below, slow surface exchange significantly affects oxygen permeability, especially for the material prepared using Method 1. The average thermal expansion coefficients (TECs), calculated from the dilatometric data, are listed in Table 1.

As for the parent compound, $\text{LaGa}_{0.80}\text{Ni}_{0.20}\text{O}_{3-\delta}$, Mg-containing composition exhibits a transition to pseudometallic behavior of the total conductivity, predominantly *p*-type electronic [11], at temperatures

Fig. 3. Temperature dependence of the total conductivity of $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ ceramics in air. Data on $\text{LaGa}_{0.80}\text{Ni}_{0.20}\text{O}_{3-\delta}$ [11] are shown for comparison.

above 1100 K (Fig. 3). Most probably, this results from oxygen losses on heating and the corresponding decrease in p -type charge carrier concentration, similar to La_2NiO_4 -based compounds [22]. When comparing $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ and $\text{LaGa}_{0.80}\text{Ni}_{0.20}\text{O}_{3-\delta}$ ceramics, one can note that incorporation of magnesium in the perovskite lattice leads to lower conductivity values and higher activation energy in the intermediate temperature range. Again, such a dependence on the acceptor doping is typical for perovskite-type phases derived from $\text{LaNiO}_{3-\delta}$ [23]. Since the concentration of trivalent nickel in such compounds cannot be increased to a considerable extent, the charge compensation occurs predominantly via oxygen vacancy formation, which causes narrowing bands and/or decreasing mobility of the electronic charge carriers [23].

Selected results on the oxygen permeation through $\text{LaGa}(\text{Ni},\text{Mg})\text{O}_{3-\delta}$ membranes with various thickness are presented in Fig. 4. The values of specific oxygen permeability $J(\text{O}_2)$, given in Fig. 4B, are related to the permeation flux density j as [8,12]

$$j = \frac{J(\text{O}_2)}{d} \ln\left(\frac{p_2}{p_1}\right) \quad (1)$$

Fig. 4. Oxygen permeation fluxes (A) and specific oxygen permeability (B) of $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ ceramics prepared by Method 2, as functions of the oxygen partial pressure gradient and membrane thickness.

where, p_1 is the oxygen partial pressure at the membrane permeate side. Since the quantity $J(\text{O}_2)$ is, by definition, proportional to $j \times d$, the specific permeability would be thickness-independent in the case of negligible effect of the processes at the membrane/gas boundaries. However, the data on $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ membranes unambiguously indicate that oxygen transport is determined by both bulk ambipolar conduction and oxygen surface exchange. The permeation fluxes decrease with increasing d , while $J(\text{O}_2)$ increases due to a decreasing role of the exchange rate. In addition, inspection of the data (Fig. 4) shows that reducing temperature below 1200 K leads to a greater limiting effect of the exchange processes. At 1073 K the permeation fluxes are almost completely controlled by the surface, being almost thickness-independent. On the contrary, at 1223 K the permeation-limiting effect of interphase exchange can be considered as rather minor, comparable to the limits of experimental error.

When analyzing the behavior of oxygen ionic conductivity (σ_o) estimated from the permeation and faradaic efficiency data (Fig. 5), one should mention that these estimates should be always lower than the true σ_o values if the overall oxygen transport is surface-limited [12,21]. The difference between the apparent and true σ_o values should thus decrease with increasing membrane thickness. Also, due to catalytically-active porous platinum electrodes on the membrane surface, the faradaic efficiency measurements often give an apparent ionic conductivity, which is closer to the true value and thus higher with respect to the permeation data [21]. These general predictions are in agreement with experimental results (Fig. 5). In the case of GNP-synthesized $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$, the surface exchange limitations to oxygen transport become insignificant when d is close to 1 mm. For the ceramics prepared by Method 1, the oxygen exchange is slower, leading to considerably lower permeation fluxes at temperatures below 1200 K (Fig. 6); the surface-unaffected σ_o values can be

Fig. 5. Membrane thickness dependence of the apparent ionic conductivity of $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ ceramics in air, calculated from the results on oxygen permeability (OP) and faradaic efficiency (FE) as described in [21]. Solid lines show the level of ionic conductivity, considered as unaffected by the surface exchange.

Fig. 6. Temperature dependence of the oxygen permeation fluxes through $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ membranes at fixed oxygen pressure gradient. Data on $\text{La}_2\text{Ni}_{1-x}\text{Fe}_x\text{O}_{4+\delta}$ ceramics [24] are shown for comparison.

obtained only when the membranes are thicker than 1.5–2.0 mm. The ionic conductivity obtained from the data on sufficiently thick membranes (Fig. 5) is very similar for both materials (Fig. 7).

Therefore, the synthesis procedure has no essential effect on the bulk ionic conductivity, but drastically influences surface exchange rate. A qualitatively similar situation was observed for $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ solid-electrolyte ceramics having grain size less than 10–15 μm [13]. As mentioned above, this behavior may result from a greater concentration of extended defects and/or from local inhomogeneities in $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ membranes prepared using Method 2. Another possible reason may refer to some Ga depletion of the material, synthesized by the standard ceramic technique,

Fig. 7. Temperature dependence of the oxygen ionic conductivity of $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ ceramics in air. Data on $\text{LaGa}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ [11] and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ [25] are shown for comparison.

due to volatilization of gallium oxide in the course of prolonged heat treatment. However, it seems unlikely that such a deviation from the nominal composition, which should be small, might lead to the significant variations of the surface exchange rate and lattice parameters, observed experimentally.

As expected, doping of $\text{LaGa}_{0.80}\text{Ni}_{0.20}\text{O}_{3-\delta}$ with magnesium considerably increases oxygen ionic transport: the ionic conductivity of $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ is higher than that of $\text{La}_{0.80}\text{Sr}_{0.20}\text{Fe}_{0.80}\text{Co}_{0.20}\text{O}_{3-\delta}$ and $\text{LaGa}_{0.50}\text{Ni}_{0.50}\text{O}_{3-\delta}$ (Fig. 7). Note that the latter composition exhibit highest oxygen permeability in $\text{La}(\text{Ga},\text{Ni})\text{O}_{3-\delta}$ system [11]. The ion transference numbers of $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ in air vary in the range from 1×10^{-3} to 5×10^{-2} at 973–1223 K, increasing with temperature; the activation energy for ionic conduction is about 150 kJ/mol (Table 1). It should also be mentioned that at temperatures above 1100 K, the oxygen permeability of $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ ceramics (Fig. 6) is comparable to that of another promising group of the membrane materials, La_2NiO_4 -based phases [22–24]. Therewith, due to lower nickel concentration in the lattice of $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$, this material is expected to exhibit a better stability under the membrane operation conditions.

4. Conclusions

Dense ceramic samples of perovskite-type $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ were prepared by two alternative techniques: the GNP and the standard ceramic synthesis route. No essential influence of the preparation method on the thermal expansion and partial ionic and electronic conductivities was found. The average thermal expansion coefficients of $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ ceramics, calculated from dilatometric data in air, are $(11.6\text{--}11.8) \times 10^{-6} \text{ K}^{-1}$ at 400–800 K and $(17.0\text{--}18.4) \times 10^{-6} \text{ K}^{-1}$ at 800–1270 K. Incorporation of magnesium in the lattice of $\text{La}(\text{Ga},\text{Ni})\text{O}_{3-\delta}$ significantly increases oxygen ionic conductivity and decreases electronic transport. At 1223 K, the oxygen permeability of $\text{LaGa}_{0.65}\text{Ni}_{0.20}\text{Mg}_{0.15}\text{O}_{3-\delta}$ membranes is mainly determined by the bulk ambipolar conduction; decreasing temperature leads to a greater limiting effect of the oxygen surface exchange. Despite moderate differences in the ceramic microstructures revealed by SEM/EDS analysis, the surface exchange of GNP-synthesized material is remarkably faster than that of membranes prepared by the standard ceramic procedure.

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References

- [1] H.J.M. Bouwmeester, A.J. Burggraaf, Fundamentals of inorganic membrane science and technology, in: A.J. Burggraaf, L. Cot, (Eds.), Elsevier, Amsterdam, 1996, pp. 435–528.
- [2] P.N. Dyer, R.E. Richards, S.L. Russek, D.M. Taylor, Solid State Ionics 134 (2000) 21.

- [3] T.J. Mazanec, Ceramic membranes I, in: H.U. Anderson, A.C. Khandar, M. Liu (Eds.), The Electrochemical Society, Pennington, 1997, PV95-24, pp.16–28.
- [4] M. Schwartz, J.H. White, A.F. Sammells, US Patent 6214757 (2001).
- [5] T.J. Mazanec, T.L. Cable, J.G. Frye, W.R. Kliewer, US Patent 5591315 (1997).
- [6] A. Atkinson, R.J. Chater, R. Rudkin, *Solid State Ionics* 139 (2001) 233.
- [7] S. Pei, M.S. Kleefisch, T.P. Kobylinski, J. Faber, C.A. Udovich, V. Zhang-McCoy, B. Dabrowski, U. Balachandran, R.L. Mieville, R.B. Poeppel, *Catal. Lett.* 30 (1995) 201.
- [8] V.V. Kharton, A.V. Kovalevsky, A.P. Viskup, J.R. Jurado, F.M. Figueiredo, E.N. Naumovich, J.R. Frade, *J. Solid State Chem.* 156 (2001) 437.
- [9] Q. Ming, J. Hung, Y.L. Yang, M. Nersesyan, A.J. Jacobson, J.T. Richardson, D. Luss, *Combustion Sci. Tech.* 138 (1998) 279.
- [10] Y. Tsuruta, T. Todaka, H. Nisiguchi, T. Ishihara, Y. Takita, *Electrochem. Solid-State Lett.* 4 (2001) E13.
- [11] A.A. Yaremchenko, V.V. Kharton, A.P. Viskup, E.N. Naumovich, N.M. Lapchuk, V.N. Tikhonovich, *J. Solid State Chem.* 142 (1999) 325.
- [12] V.V. Kharton, A.A. Yaremchenko, A.V. Kovalevsky, A.P. Viskup, E.N. Naumovich, P.F. Kerko, *J. Membrane Sci.* 163 (1999) 307.
- [13] G.M. Christie, F.P.F. van Berkel, *Solid State Ionics* 83 (1996) 17.
- [14] V.V. Kharton, V.N. Tikhonovich, L. Shuangbao, E.N. Naumovich, A.V. Kovalevsky, A.P. Viskup, I.A. Bashmakov, A.A. Yaremchenko, *J. Electrochem. Soc.* 145 (1998) 1363.
- [15] V.V. Kharton, E.N. Naumovich, A.V. Kovalevsky, A.P. Viskup, F.M. Figueiredo, I.A. Bashmakov, F.M.B. Marques, *Solid State Ionics* 138 (2000) 135.
- [16] V.V. Kharton, F.M. Figueiredo, A.V. Kovalevsky, A.P. Viskup, E.N. Naumovich, A.A. Yaremchenko, I.A. Bashmakov, F.M.B. Marques, *J. Europ. Ceram. Soc.* 21 (2001) 2301.
- [17] V.V. Kharton, A.V. Kovalevsky, A.A. Yaremchenko, F.M. Figueiredo, E.N. Naumovich, A.L. Shaula, F.M.B. Marques, *J. Membrane Sci.* 195 (2002) 277.
- [18] M.W. Murphy, T.R. Armstrong, P.A. Smith, *J. Am. Ceram. Soc.* 80 (1997) 165.
- [19] Y.-J. Yang, T.-L. Wen, H. Tu, D.Q. Wang, J. Yang, *Solid State Ionics* 135 (2000) 475.
- [20] J. Rodriguez-Carvajal, *Physica B* 192 (1993) 55.
- [21] V.V. Kharton, A.P. Viskup, A.V. Kovalevsky, F.M. Figueiredo, J.R. Jurado, A.A. Yaremchenko, E.N. Naumovich, J.R. Frade, *J. Mater. Chem.* 10 (2000) 1161.
- [22] V.V. Vashook, N.E. Trofimenko, H. Ullmann, L.V. Makhnach, *Solid State Ionics* 131 (2000) 329.
- [23] V.V. Kharton, A.A. Yaremchenko, E.N. Naumovich, *J. Solid State Electrochem.* 3 (1999) 303.
- [24] V.V. Kharton, A.P. Viskup, E.N. Naumovich, F.M.B. Marques, *J. Mater. Chem.* 9 (1999) 2623.
- [25] V.V. Kharton, A.V. Kovalevsky, A.P. Viskup, A.L. Shaulo, F.M. Figueiredo, E.N. Naumovich, F.M.B. Marques, *Solid State Ionics*, 2002, in press.