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Design of Multilayer Ceramic MIEC Membranes

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Abstract: The development of multilayer mixed conducting oxide membranes on porous dead-end tubular mineral-based glass-ceramic supports is presented. Nanopowders of compatible complex perovskites and fluorites as membrane materials were obtained by mechanochemical synthesis. The deposition of oxide ceramic porous and dense layers was carried out by casting of slurries in organic medium, prepared from narrow fractions of agglomerated powders. A linear dependence between the sintering temperature T_s and calculated effective melting point T^*_m for complex perovskites and fluorites was revealed that allowed to propose a simple rule for the synthesis of complex oxides with required T_s. Dead-end tubular supports were produced by casting from selected kaolins with organic/inorganic additives. The misfit in sintering temperatures of porous substrate and MIEC ceramic layers was eliminated by modification of substrate and heavily doping of mixed oxides. The elimination of shrinkage misfit between the porous substrate and ceramic layers was achieved by optimization of operation conditions and compositions of both substrate and ceramics. Almost gas-tight cost efficient catalytic membrane reactors CMRs with large operation surface $\sim$30 cm^2 and good prospects for up-scaling were produced and tested.

Keywords: Multilayer MIEC ceramic membrane, CMR, mechanochemical synthesis, POM

INTRODUCTION

The key to success of the permselective membrane technology of methane transformation into high-purity syngas by using oxygen separated from air

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is to develop the cost-efficient catalytic membrane reactor (CMR) which combines a high oxygen permeability with a long-term mechanical and phase stability in the hostile syngas environment at elevated temperatures. Dense MIEC ceramic membranes are well-known to have a great potential for catalytic high-temperature processes including methane reforming (1). While bulk diffusion limits the oxygen permeability for thick membranes, the kinetics of the surface processes on both membranes sides becomes the rate-limiting for thin membranes (2). Supporting a (micro)porous oxide layer with a high rate of O_2 activation on a dense non-porous MIEC layer membrane or using a microporous MIEC substrate is known to increase the oxygen flux (3–9). A new strategy for the development of CMR based on multilayer membranes prepared by casting technology from strongly agglomerated mechanochemical nanopowders was proposed recently (9). The problem of shrinkage misfit between ceramic layers may be easily solved due to close values of shrinkages for different "mechanochemical" powder fractions. This peculiarity as well as a high sintering ability of "mechanochemical" powders is related to a high content (~10%) of vacancies. A coarse fraction of agglomerates with a mean size of particles ~50 μm was used for the production of a porous support with ~1 mm thickness (9, 10). However, the ~20% yield of coarse fraction after mechanosynthesis and separation of nanopowders is too small. In such a case, the cost of ceramic membranes and CMR manufacturing is mainly determined by rather high nanopowder consumption for support production. Moreover, the slurry comprised of large agglomerates is not sufficiently stable by itself; hence, an organic medium possessing simultaneously a high viscosity and volatility is required. Fabrication of a porous tubular support for CMR from the coarse fraction of agglomerates becomes a formidable problem. The ideal solution is to use an inert macroporous substrate on which one deposits consecutively MIEC layers with graded porosity and chemical composition ending with a thin dense MIEC film with supported catalyst (10, 11), (Fig. 1). Combination of meso-and micro-porous MIEC layers with a thin gas-tight layer provides a maximal oxygen flux under mixed surface exchange kinetics/bulk diffusion control.

This paper describes design of such multilayer ceramic membranes based upon the dead-end inert tubular macroporous support derived from kaolins. Low-cost tubular porous mineral-based ceramic supports for membranes were proposed recently (12–17).

High membrane durability may be achieved by optimization of the chemical composition of materials and decreasing operation temperatures due to improved performance and architecture. The most appropriate for laboratory studies dead-end tubular form of CMR may be obtained by casting technology with the use of natural kaolin nanopowders. Such a form of CMR provides a fast testing due to easy solution of a difficult problem of sealing. Simple techniques of membranes manufacturing and minimal consumption of expensive reagents result in cost efficiency. In addition, the

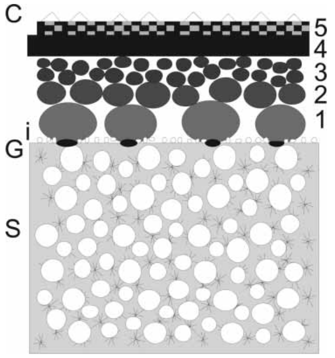

Figure 1. Multilayer membrane. S-macroporous substrate, i-interlayer, C-finely dispersed catalyst, G-glass, 1-3 porous MIEC ceramic layers, 4-dense MIEC ceramic layer, 5-protective MIEC composite layer.

proposed approach permits up-scaling of CMR by using the same materials and operations.

EXPERIMENTAL

For the preparation of single phase powders with perovskite or fluorite structure, mixtures of simple oxides were treated in laboratory planetary mill AGO-2 for 20–30 min. The mass of chromium steel balls (10 mm diameter) was 220 g, while the mass of powder mixtures was about 15 g. The phase characterization of powders was carried out by XRD using Cu-K_α radiation. A special procedure of the mechanical treatment was used to decrease drastically powders contamination by iron and to enhance their phase and size uniformity (18). Mean crystallite sizes estimated from the XRD peaks broadening were within 20–50 nm. After milling, the powders were separated into relatively narrow fractions by using electro-mass-classifier (EMC) technique and by sieving (19). The ethanol-based slurries of mixed oxide powders were prepared with addition of 2–4% polyvinylbutyral or some natural binders. The estimated green relative density of deposited films was within 46–54%.

The clay-water slurries were prepared on the bases of available kaolins from Ukrainian and Russian deposits with the addition of sodium electrolytes. Additives in slurries of 20–50% microcrystal cellulose (MCC) and 1–10% $Al(OH)_3$ (Gibbsite) powder comprised of 1–10 μm platelet-like particles were used to increase the porosity and to enhance the thermal stability. The green dead-end tubes obtained by casting of slurries into gypsum forms with subsequent drying, were calcined at $T_g = 850–1000°C$ before leaching. Leaching of macro-porous metakaolinite substrate was carried out in acid (pH$\sim$2) solutions to increase porosity and thermal stability at sintering temperature T_s. Supports were modified as well by alumina- or zirconia sols. Procedures of the preparation of porous substrates compatible with MIEC ceramics are available in details elsewhere (17). An intermediate layer has been deposited on the inner-side of dead-end tubes by ethanol-based slurry of α-Al_2O_3 (a mean particle size $\sim$44 nm) and then pre-sintered at $T_p = 950-1100^\circ C$. The open porosity of supports was estimated from the water uptake. Ceramic layers were fixed by annealing at different temperatures. A mean thickness of each oxide ceramic layer was estimated from the values of the inner surface of the tubular porous support, a theoretical density of the complex oxide and deposited mass of a material. CMR's were heated to room temperature to sintering T_s 1360–1380°C with a rate $\sim$10 K/min and kept at this temperature for 1 min.

The testing of CMR's has been carried out in the installation equipped with an IR absorbance gas analyzer PEM-2M and an electrochemical H_2 detector with data acquisition and processing through a PC (9).

RESULTS AND DISCUSSION

A scheme of the developed multilayer functionally-graded membrane for high temperature catalytic processes is shown in Fig. 1. A typical thickness of substrate is $\sim$1 mm, 1st ceramic layer $\sim$60 μm, 2nd layer $\sim$30 μm, 3rd layer $\sim$15 μm, 4th layer $\sim$5 μm, and protective 5th layer $\sim$2 μm. The particles size distribution of strongly agglomerated "mechanochemical" nanopowders and used fractions are shown in Fig. 2. An intermediate α-Al_2O_3 layer is introduced to prevent too strong a chemical reaction between ceramics and silica glass in substrate. A top protective layer of MIEC membrane is comprised of the fluorite- and perovskite-like phases composite ensuring an enhanced stability at a feed side relative to single phase perovskites (20, 21).

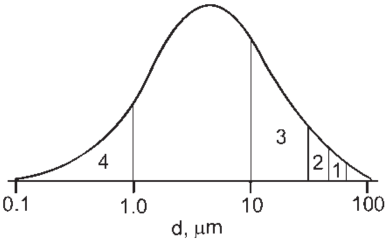

Figure 2. Typical particle sizes distribution for mechanochemical nanopowders. No of fraction corresponds to No of ceramic layer in Fig. 1.

The flow-sheet of multilayer CMR preparation consists of operation sequences S (substrate) and C (ceramics) of preliminary preparation of components for CMR, and sequence R (reactor) of CMR fabrication.

S-sequence includes the next steps: preparation of a blend from selected kaolins and clays → washing from soluble salts → sieving → preparation of slurry with addition of Na-electrolytes by ball milling and/or ultrasonic treatment → ageing → introduction of organic/inorganic additives → degassing by vacuum treatment → casting in gypsum forms → drying of dead-end green tubes → firing at T_g → leaching in acid water solution → washing → drying → modification by sol → drying → deposition of interlayer by casting (variant: simultaneously with impregnation by salts) → pre-sintering of supports at T_p → selection of suitable supports. The key factors in S-sequence were determined (11–22):

1) selection of raw materials;
2) type and quantity of organic burning additives;
3) conditions of pre-firing and related parameters of leaching;
4) sol modification of metakaolinite;
5) thickness of interlayer.

C-sequence includes the next operations: preparation of blends for different ceramic layers from simple oxides (variant: blends of salts previously calcined to remove the gases) → mechanochemical synthesis → separation in fractions → sieving and refinement of powder fractions for porous/dense ceramic layers with recycling of residues → preparation of ethanol-based ceramic slurries. The key factors in C-sequence are related to synthesis of complex oxides with desired temperature of sintering to avoid shrinkage misfit between different ceramic layers. The other difficult problem is related to a low stability of slurries containing large agglomerates.

R-sequence includes the next operations: deposition of the 1st perovskite ceramic layer from large agglomerates onto the inner side of dead-end tubes by casting of ethanol-based slurry → pre-sintering at T_{ps} to fix large agglomerates in the surface of support → deposition of the 2nd perovskite ceramic (mesoporous) layer by casting → drying at elevated T → deposition of the 3rd perovskite ceramic (microporous) layer → drying → deposition of the 4th perovskite ceramic gas-tight layer → drying → deposition of protective composite ceramic layer → final sintering at T_s → room T testing of reactors for non-selective permeability of air into He flow → deposition of finely dispersed catalyst → fixing of catalyst by firing at T_c ($<T_s$) → testing of CMR's in reaction of partial oxidation of methane. The key factors in R-sequence are related to deposition of the 1st ceramic monolayer from large agglomerates and conditions of final sintering. Important problems are the development of the catalyst providing a high selectivity of reaction, and procedure of its deposition/fixing. However, the last operation has a sense only after complete development of CMR with gas-tight membrane.

The optimization of a large number of parameters in the proposed flow-sheet may be executed step by step to achieve compatibility of membrane materials in T_s, shrinkage curves, chemical compatibility, and coefficients of thermal expansion. For instance, the main problem–a great difference in T_s for the porous substrate (~1300°C) and the best conductors (~1400–1500°C), was solved in (9) by means of sintering aid (Bi_2O_3). However, this solution has a severe drawback due to formation of glass with a low "melting" point at the ceramics/support interface (Figs. 1, 3). An excessive formation of glass in the interface region results in the degradation of perovskite ceramics, cracking of the membrane, and closing of the open porosity in substrate. To increase the thermal stability of a porous substrate, about 30 iterations were made in (17) for the selection of suitable

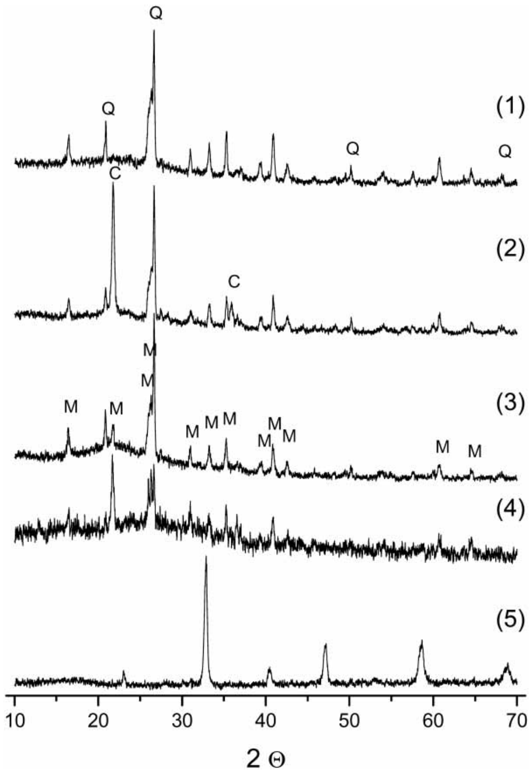

Figure 3. X-Ray diffraction patterns (CuK_α) of annealed samples: (1) substrate from selected raw materials, T = 1260°C (Q- quartz, M- mullite and glass); (2) metakaolinite after leaching and firing at T = 1050°C (C- crystobalite, mullite and glass); (3) sample 2 after firing at T = 1260°C (quartz, mullite, glass); (4) product of interaction between substrate and complex perovskite at 1260°C (glass and remnants of mullite); (5)–complex La-Sr-Co-Fe (LSCF) perovskite, T = 1260°C.

clays/kaolins and for determination of compositions for water-clay slurries with good casting properties. The key requirements to raw materials were formulated:

1) a minimal content of phase impurities (quartz, illite, etc);
2) weakly expressed thixotropy (a change of suspension viscosity during casting in gypsum form);
3) efficient peptization after addition of Na-electrolytes;
4) good mechanical strength of green bodies. Required open porosity (>25%) and shrinkage (~15%) for porous substrate after firing at ~1400°C were obtained for compositions on the base of Prosianovski kaolin (Ukraine) with 40% additive of MCC after leaching of metakaolinite, Fig. 3.

Additional modification of substrates by a zirconia sol in the stage of metakaolinite allows to minimize the shrinkage misfit ΔS between the substrate and ceramics during sintering, Fig. 4. In the case of $\Delta S > 2\%$ a wavy relief of ceramics was obtained which inevitably leads to cracking during subsequent operations. In the case of $\Delta S < -1\%$ the formation of cracks in ceramic membranes is inevitable during sintering. The acceptable range of the shrinkage misfit is $1\% > \Delta S > 0$, where conditions of sintering are like 2-dimensional hot pressing favoring formation of gas-tight ceramics. Due to some anisotropy of shrinkage of supported ceramic films, the range of suitable ΔS values is slightly extended.

Firing and leaching are the key operations of importance in the preparation of a suitable substrate. Firing of kaolinite (the main mineral of kaolin) at

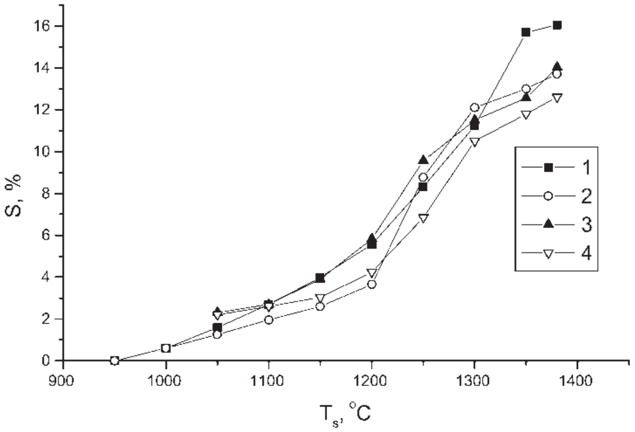

Figure 4. Shrinkage curves for complex perovskite on the base of LSCF in a form of a disk (1), substrate on the base of selected kaolin after leaching in a tubular form (2), substrate 2 after additional Zr-sol modification (3), substrate 2 after additional Al-sol modification (4).

optimal $T_g = 950-1000°C$ leads to formation of metakaolinite according to equation:

$$Al_2Si_2O_5(OH)_4 \rightarrow Al_2Si_2O_7 \quad (1)$$

Firing at lower temperatures leads to a low mechanical strength of tubes and a low selectivity of consequent leaching in diluted solutions of HCl and HNO_3. On the other hand, firing at higher temperatures results in very slow leaching of glass-forming ions like Na^+, K^+, Ca^{2+}, Fe^{n+}. Metakaolinite undergoes decomposition after firing at $T>1000°C$ (Fig. 2) with the formation of nanocomposite–mullite fibers reinforced silica glass:

$$3Al_2Si_2O_7 \rightarrow Al_6Si_2O_{13} + 4SiO_2 \quad (2)$$

Silica possesses a high reactivity to some oxides due to formation of a silica glass with a low "melting point". It is a clear drawback of the proposed substrate, but the number of advantages overrides the visible negative consequences. To diminish the formation of glass to a tolerable level (without a good contact of ceramic layer with substrate, delamination and cracking of ceramic films take place), a balanced combination of different operations is required: the addition of mullite or $Al(OH)_3$ in water-clay slurry for binding a part of SiO_2; optimization of interlayer thickness (Fig. 1); decreasing the content of glass-forming oxides in the 1st layer; selective leaching of silica from the inner side of tubes in HF solutions. Other complicated problems related to silica in substrate is a great difference in behavior of crystalline and glass materials during thermal treatment (23). To minimize this drawback, a high temperature of the final sintering (~1400°C) greatly exceeding that of the CMR operation temperature (~800°C) and modification of the substrate by a sol are required.

To provide a compatibility of materials in the multilayer membrane by creation of an adjusted gradient of chemical compositions in the usual way, it is necessary to test a number of novel complex compositions with unknown "melting" point T_m and unpredictable T_s. For tailored synthesis of fluorites and perovskites with required T_s, it is quite necessary to find a simple empirical rule for its estimation. To solve this problem, sintering of nanopowders obtained via mechanosynthesis in similar conditions was studied in 32 systems including potential membrane materials. For data comparison, the linear shrinkage value 12% was taken as an optimal parameter of sintering. Temperatures T_s required for achieving this shrinkage were estimated by extrapolation of experimental data obtained at 4 different temperatures. After the elimination of all extraneous factors affecting the sintering of ceramics (24), satisfactory linear correlations between T_s and effective melting point T_m^* calculated from T_m of constituent simple oxides were obtained for complex fluorites ($r = 0.86$) and perovskites ($r = 0.76$) with formula $A_xB_y\ldots$ ($T_m^* = x \cdot T_{mA} + y \cdot T_{mB} + \ldots$, $x + y + \ldots = 1$), Fig. 5. The sintering temperature T_s for fluorites is higher for ~100 K than for

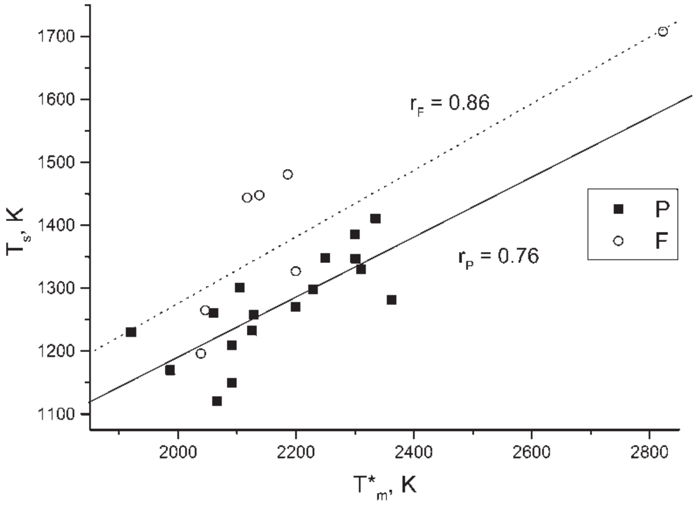

Figure 5. Relation between T_s (S = 12%) and T^*_m for complex perovskites (P) and complex fluorites (F).

perovskites with the same T^*_m. According to the formulated rules, new compatible complex oxides with required T_s were prepared for multilayer membrane fabrication with a relatively small content of expensive reagents. Some rules for the preparation of a chemically compatible fluorite + perovskite composites for a protective layer were formulated recently (20).

Using the above proposed approaches, about 200 reactors were fabricated, Fig. 6. Among them, ∼10 reactors were produced with almost gas-tight ceramic membranes and nonselective room temperature air leakage into the He stream was less than 1%. Taking into account a relatively large

Figure 6. Porous tubular/dead-end tubular supports and CMR obtained by casting technology.

Table 1. The methane conversion tests for CMRs with deposited catalyst

		Input[a] content (%)		Output content at 880°C (%)						CH_4 conversion (%)	
CMR no	Catalyst	CH_4	O_2	CO_2	CO	H_2	H_2O	O_2	CH_4	Total	To syngas
19	$Pt/Ce_{0.45}Zr_{0.45}La_{0.1}O_2$	3.4	1.7	0.72	0.42	0.92	1.5	0.43	2.33	31	16
75	-II-	3.0	0.7	0.38	0.16	0	1.34	0.67	1.3	57	0
110	$Pt/LaNiO_3/Ce_{0.4}Zr_{0.4}La_{0.2}O_{2-x}/$	1.0	0.5	0.40	0.03	0.01	—	0.62	0.55	45	2
110	+ microspherical catalyst $Pt/LaNiO_3/Ce_{0.4}Zr_{0.4}La_{0.2}O_{2-x}/\gamma\text{-}Al_2O_3$	1.0	0.5	0.16	0.60	0.65	—	0.22	0.30	70	60

[a] 1–4% CH_4 in He; flow 2.78 cm^3/s.

(~30 cm^2) operation surface of CMR's, one can suppose a causal formation of cracks. In other words, operation parameters in R-sequence of the flow-sheet play an important role in reproducible preparation of CMR's. The study of membranes by optic microscopy revealed that formation of large glass fields at the interface is the main cause of cracking. This conclusion is confirmed independently by characteristic noise accompanying cooling of CMR's.

Preliminary results of tests for some reactors in the partial oxidation of the methane (POM) process were obtained, Table 1. As a rule, tests show a relatively low selectivity to partial oxidation reaction, especially for reactors with the top layer from LSGM-based perovskites. Rather good results were obtained for reactors with a protective layer which comprised of ceria-based composites and catalysts developed in (25). A microspherical catalyst loaded into the CMR strongly improved syngas selectivity of POM process. The optimization of catalysts and procedures of its deposition on multilayer membranes are in progress.

CONCLUSIONS

An optimum cost-efficient architecture of the MIEC membrane with selective oxygen permeability is proposed for POM and related processes. The flow-sheet of production of multilayer oxide ceramic/composite membrane with gradients of chemical compositions and porosity in layers applied on the macroporous dead-end, tubular, mineral-based glass-ceramic supports is developed. Casting of slurries has been used for deposition of thin ceramic layers. Key factors are determined for further fine tuning of membranes' design. To control the shrinkage misfit between layers, a set of approaches was used including a modification of substrate and optimization ceramics compositions. Mechanochemical synthesis of complex oxides in the form of strongly agglomerated nanopowders and their separation into fractions is a promising technique for preparation of compatible membrane materials. For relative estimation of T_s for novel complex oxides with fluorite- and perovskite-related structures, a simple rule is proposed based on the linear correlation between the calculated effective melting point T_m^* and experimental T_s. About a dozen dead-end tubular CMR's have been fabricated with an almost gas-tight membrane for POM and related processes. The proposed architecture of multilayer CMR allows correct and fast testing of membrane materials and catalysts for POM reaction. Rather good results were obtained for the ceria-based composite protective top layer.

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