



Asymmetric supported dense lanthanum tungstate membranes

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Abstract

In this work, a colloidal processing route for dense asymmetric $\text{La}_{28-x}\text{W}_{4+x}\text{O}_{54+3x/2}$ membranes for hydrogen gas separation applications was established. Dip coating process conditions were optimized to obtain $\approx 20\ \mu\text{m}$ thick dense layer supported on a porous substrate of the same composition. Surfactants based on electrosteric stabilization were evaluated to obtain stable suspensions in ethanol. The effect of the quantity and type (rice starch and carbon black) of sacrificial pore formers was evaluated for the porous substrates. Based on our results, samples made with 35–45 vol.% carbon black are the best choice to obtain highly porous supports with the optimum characteristics for the fabrication of asymmetric membranes.

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1. Introduction

Lanthanum tungstates, $\text{La}_2\text{O}_3:\text{WO}_3$ (LWO) with a molar ratio $\sim 3:1$, have attracted attention due to their relatively high mixed proton-electron conductivity at high temperatures and good stability in moist CO_2 environment making them an interesting material for dense hydrogen permeable membranes.^{1–5} Especially the compositions $\text{La}_{28-x}\text{W}_{4+x}\text{O}_{54+3x/2}$ ⁶ giving La:W ratios in the range 5.6–6 have been carefully studied. $\text{La}_6\text{WO}_{12}$ exhibits n- and p-type electronic conductivity under reducing and oxidizing atmospheres at high temperatures, respectively, determined from electrical measurements by Haugsrud et al.^{3,4} In our previous work⁵ on hydrogen permeation in asymmetric $\text{La}_{28-x}\text{W}_{4+x}\text{O}_{54+3x/2}$ ($x = 1.22$, La:W ratio ~ 5.6) membranes it was established that the defect situation is not the same in the whole temperature range up to $1000\ ^\circ\text{C}$. At $800\text{--}850\ ^\circ\text{C}$ there is a shift, where below that temperature the permeation is limited by n-type conductivity and above by proton conduction.

Further, adding water vapor enhances the hydrogen permeation at temperatures above $950\ ^\circ\text{C}$.⁵

In order to assess the true potential of these materials it is important to measure hydrogen permeation directly on thin supported membranes, as permeation estimates from conductivity data often are based on simplified models and permeation measurements on thick samples can conceal possible surface kinetic limitations.⁷ For industrial applications of LWO-based materials, asymmetric membranes are also the preferred geometry to achieve high enough hydrogen permeation. However, works reported on the colloidal fabrication of lanthanum tungstate thin films are scarce, and it is therefore a need to define the processing route conditions for this novel material. Apart from challenges to maintain desirable LWO stoichiometry, the processing route should be cheap and industrially scalable due to economical/applicability concerns. Ceramic consolidation routes based on colloidal processing are widely used within the technical ceramic industry and are based on stable ceramic oxide particle suspensions in aqueous or organic media.⁸

In this work, asymmetric membranes based on lanthanum tungstate with composition $\text{La}_{28-x}\text{W}_{4+x}\text{O}_{54+3x/2}$ ($x = 1.22$, La:W ratio = 5.6), hereinafter denoted as LWO56, were fabricated by colloidal processing. A processing route based on dip coating of $\sim 20\ \mu\text{m}$ LWO56 dense membrane on porous LWO56 supports was developed. The quantity and type of sacrificial pore

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Table 1
Compositions of slurries used for dip coating of the porous LWO56 bond layer and their viscoelastic parameters.

Slurry code	Carbon black (wt.%) ^a	PVB (wt.%) ^b	LWO56 (vol.%)	Solid content (vol.%)	Rheological parameters		
					Storage modulus, G' (mPa)	Flow point, τ_f (mPa)	Yield point, τ_y (mPa)
BL20-1			4.5	7.4	892	78.5	26.9
BL20-2			2.25	3.7	857	14.4	3.4
BL20-3	20	2	1.97	3.24	239	11.1	2.9
BL20-4			1.78	2.74	–	–	–

^a Of LWO56 powder.

^b Of total solid load.

formers such as carbon black and rice starch within porous LWO56 supports was assessed. The deposition of a dense layer by dip coating of a colloidal suspension on highly porous support should address the issue of highly irregular surface topography of the support. The irregular surface is caused by the use of pore formers resulting in holes and defects on the substrate surface that cannot be covered efficiently by relatively thin dense functional layer. To smoothen the surface of the porous support and ensure gas tightness of the asymmetric membrane, a porous bond layer between the porous structural support and the dense membrane layer was adapted.

2. Material and methods

2.1. Asymmetric membrane preparation

The lanthanum tungstate powders were synthesized by spray pyrolysis and different heat treatments (700 or 1000 °C) were done in order to obtain powders with different characteristics. Detailed synthesis procedure was reported previously.⁹ Powders with specific surface area of ~ 6 and ~ 9 m²/g and average particle size, $d_{V50} = 900$ nm and 400 nm were used as starting materials for the porous support/bond layer and dense layer, respectively.

Porous supports (25 mm diameter, 2 mm thickness) were uniaxially pressed with the addition of pore formers (35–52 vol.%) and consequently calcined and presintered prior to dip coating (detailed conditions are discussed in Section 3). The LWO56 powder and pore former mixtures were homogenized in ethanol by ball milling for 15 min. Two commercially high purity pore formers with different particle shape, particle/agglomerates sizes and decomposition temperatures were compared: rice starch (DR-LA, REMY industries) and carbon black (charcoal activated, Merck Chemicals KGaA).

Slurries for dip coating of the porous bond layers were prepared in two steps. In the first step, LWO56 powders, carbon black as pore former and polyvinyl butyral (PVB) as the binder were dispersed in ethanol and ball milled for 24 h in order to obtain a homogeneous distribution of the constituents. In the second step (and prior to rheological characterization) the suspensions were slowly rolled (Roller mixer RM10W CAT, Staufen, Germany) for 24 h to age them and eliminate air bubbles. The slurry compositions (Table 1) with varying solid

content of ceramic powders, pore former and binder content were evaluated.

Suspensions for dip coating of dense layers (2 vol.% solids) were prepared by ultrasonically dispersing LWO56 powders with varying surfactant content (0.5–3.5 wt.% of LWO56) in pure ethanol. Two electrosteric surfactants were studied: surfactant 1 – polymer with polar groups (Dolacol D 1003, Zschimmer & Schwarz GmbH) and surfactant 2 – short chain polar surfactant (acetic acid, Sigma Aldrich).

The dense layer deposition (and porous bond layer if needed) was performed by dip coating during 10 s holding time (5 s for porous layer) with immersion and pulling out speeds within the range of 1–2 mm s⁻¹. Prior to dip coating the suspensions for the dense layers were diluted to 0.75 vol.% of solid content. After each coating step, the sample was presintered at 1100 °C for 1 h using 2 °C/min heating and cooling rates. When the porous bond layer was deposited an additional calcination process was carried out; more details about this step are given later. Two coating-presintering cycles were needed to achieve the desirable thickness of the dense membrane layer.

The asymmetric membranes were co-sintered in one step at 1420 °C for 3 h in ambient air (2 °C/min). These conditions ensured suitable characteristics of the LWO56 material for the use as a membrane: single phase, full densification with homogeneous microstructure and no exaggerated grain growth.⁹

2.2. Characterization

The decomposition temperature of the pore formers was studied by thermal analysis up to 1000 °C in air with a heating rate of 5 °C/min (STA 449C, Netzsch, Selb, Germany). The morphology of the pore former powders dispersed in ethanol was compared by scanning electron microscopy (SEM, Hitachi S3000N). Particle size distribution was carried out in aqueous media by laser diffraction analyzer (Mastersizer 2000, Malvern Instruments, UK). Porosity of the sintered porous supports was obtained from density measurements by Archimedes method in 2-propanol. SEM images were also used for the estimation of porosity as well as for pore size distribution by image analysis using the high degree of contrast between the dark pores (voids) and highly reflective LWO56 material. Prior to SEM analysis, the samples were vacuum imbedded with a low density resin (Epofix Struers, USA) and cured for 24 h at 60 °C, followed by polishing with 9, 3 and 1 μm diamond suspension.

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