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Preparation, characterization and stability of vanadium/Y_2O_3-stabilized ZrO_2 composite membranes under different atmospheres

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ABSTRACT

In this experimental work vanadium/Y_2O_3-stabilized ZrO_2 composite membrane was successfully fabricated by a two-step sintering process. The formation of a well-defined ceramic metal composite membrane was confirmed under high vacuum sintering conditions. Their surface morphology, stability and structural properties were studied as a function of temperature up to 1100 °C by thermogravimetry, differential thermal analysis, scanning electron microscopy, energy dispersive X-ray spectroscopy, and X-ray diffraction analysis. Significant differences were observed in the crystalline structure of the vanadium/Y_2O_3-stabilized ZrO_2 composite membranes when they were treated at high temperature in different atmospheres (vacuum, air, hydrogen, nitrogen, and helium). The first hydrogen permeation investigation of vanadium/Y_2O_3-stabilized ZrO_2 composite membrane is reported. Preliminary hydrogen permeation experiments have been confirmed that hydrogen flux was 1.08 ml min^{-1} cm^2 for a dense vanadium/Y_2O_3-stabilized ZrO_2 composite membrane (thick: 380 μm) at 300 °C using 100% H_2 as the feed gas. Both high temperature XRD and *ex situ* study showed deterioration of membranes and the formation of a small amount of vanadium nitride (VN_x) and vanadium hydride (VH_x) solid solutions under nitrogen and hydrogen gas conditions, respectively.

1. Introduction

Hydrogen production is a key component of a fuel-cell hydrogen economy. Inorganic membranes for pure hydrogen production and purification are a key technology in the strategy to develop more environmentally friendly power sources [1]. As a result, considerable interest has arisen in the research area of high performance hydrogen membranes under the severe conditions typical of gasification of fuels reforming or hydrogen production.

For the production of hydrogen, diverse methods and sources are available [2–5]. Large amounts of data on hydrogen permeation through inorganic membranes of varying composition have been reported by J. Sunarso et al. [6], Lu et al. [1], and Kikuchi [7]. In addition to its potential role in generating fuel-cell hydrogen and gas purification, the water–gas shift (WGS) reaction have current importance in several commercial operations [8].

The literature on palladium is extensive. Over the last decade, researchers have focused on thin palladium membranes supported by porous substrates and ceramic metal composite membranes for high-pressure, high-temperature applications, as well as the development of other metal–palladium alloy systems [9]; nevertheless, recent efforts in the hydrogen purification and separation membrane have focused on the development and evaluation of non-palladium based membranes that offer a lower cost, high flux, and high durability [10].

A critical component within a membrane reactor unit is the membrane stability behavior against different atmospheres. Hydrogen extraction, in particular, requires high-quality membranes that should exhibit high thermal-chemical stability. Despite this, the effect of changing the atmospheric gas on non-palladium based membrane material properties has been scarcely studied.

According to the recent work reported in the literature, the point is that for the middle temperature in the region of 300–600 °C, the crystalline and amorphous palladium or palladium-alloy membranes have been researched extensively to get high flux and solve the hydrogen embitterment of palladium because it is common knowledge that the main disadvantages of this material are its low stability for feedstock poisons such as carbon monoxide, carbon dioxide, ammonia or hydrogen sulfide [11], and its high cost [10]. Exhaustive background reviews of the main limitations of Pd-based membranes for hydrogen separation were recently prepared by Lu et al. [1] and Armor [12].

Alternatively, metals from the Group V including vanadium are currently being evaluated by various investigators because

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Table 1
Coefficient of thermal expansion (TEC) of selected hydrogen permeability metal to Y_2O_3-stabilized ZrO_2 ceramic phase and some other selected solid oxide ionic conductors.

Metal	Temperature (K)	α ($\times 10^{-6}$ K^{-1})	Ref.
Vanadium	600	10.2	[26]
	700	10.5	[26]
	1000	11.6	[26]
Palladium	600	13.6	[26]
	700	14.1	[26]
	1000	15.6	[26]
ZrO_2 stabilized with 8 wt% Y_2O_3	298–1273	10.5	[27]
$Ce_{0.8}Sm_{0.2}O_{2-\delta}$	298–1273	12.3	[28]
$Ce_{0.8}Gd_{0.2}O_{2-\delta}$	300–1050	11.5	[29]

these alloys have shown some promise in comparison to palladium [13,14]. For example, Group V elements have over an order of magnitude more permeability for hydrogen than palladium [15–17]. As matters stand, the group V elements have a very high solubility for H_2 resulting in a high H/Metal ratio during hydrogen permeation, which can lead to embitterment of the metal that may lead to subsequent cracking of the membrane [18]. Hydrogen permeation is a consequence of the dissolution and diffusion of hydrogen in the dense membranes, and it can be strongly influenced by interactions that occur at material surface and/or at interfaces between metal and another phase components on ceramic metal composite membranes [19–23]. Van Deventer et al. [19] and Namba et al. [21] reported that the surface impurity layers on the pure vanadium membrane give a significant influence on its hydrogen permeation properties and could be well described using an oxide barrier model in according to the study by Strehlow and Savage [23].

Additionally, the value of the thermal expansion coefficient (TEC) should match with those of the other membrane components. In fact, it is well known that the TECs of the different components must be as close to one another as possible in order to minimize thermal stresses which could lead to cracking and mechanical failure. The reason for this possible outcome is the fact that if the various metal and oxide components in a ceramic metal composite membrane are mismatched in thermal expansion characteristics, the membranes can crack during thermal cycling and render the ceramic metal composite membrane ineffective or at least less effective.

In searching for a support which will be compatible with high-permeability vanadium-based membrane, it is deliverable to minimize stress at the metal vanadium interfaces which can lead to the formation of cracks. For the most part, stress at the interface can be minimized if the material components of ceramic metal composite membrane have similar TEC over the anticipated temperature range of composite membrane fabrication and use. As a matter of fact, we noted that high-permeability vanadium-based membrane (i) exhibited high hydrogen conductivity in a relatively low-temperature range around 300–500 °C [24] and (ii) the TEC values consistent with 8 mol% Y_2O_3-stabilized ZrO_2 ceramic phase. In fact, the TECs for both phases are nearly equal to about $10.5 \times 10^{-6}\,K^{-1}$ [25,26], whereas especially remarkable is the fact that the TEC results on palladium (*i.e.*, $14.1 \times 10^{-6}\,K^{-1}$ at 700 K) [25] are quite different from those of the Y_2O_3-stabilized ZrO_2 ceramic phase, or other selected ionic conducting oxide (Table 1). In addition, it is also important to note that TECs of $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ [27] and $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ [28] are higher than that of the vanadium phase. Briefly, we hypothesize that the ceramic metal composite membrane stability is governed not only by intrinsic mechanical resistance of single membrane components (*i.e.* metallic vanadium or Y_2O_3-stabilized ZrO_2 ceramic phase) in different gas, but also by thermalstructural stability at the ceramic/metal interfaces.

The present paper has three objectives. First, we provide the first description of the novel dense vanadium/Y_2O_3-stabilized ZrO_2 composite membranes for hydrogen production, separation and related processes. It is believed that it is a new idea about vanadium-based composite membrane and a novel and unique engineering approaches in response to current energy issues. Our hypothesis is supported by the fact that vanadium TEC is coincident with Y_2O_3-stabilized ZrO_2 ceramic phase on the required temperature range. The second, to give an overview of the preparation and characterization of dense vanadium/Y_2O_3-stabilized ZrO_2 composite membrane were carried out under different atmospheric conditions. Therefore, the purpose of this study was also to investigate the stability of metallic vanadium in a new palladium-free composite membrane under different atmospheric condition. The last is to examine some questions concerning the membrane performance. We also compare hydrogen flux measurements from dense vanadium/Y_2O_3-stabilized ZrO_2 composite membrane with published measurements from other palladium-free ceramic metal composite membranes.

2. Experimental

2.1. Sample preparation

A 60 vol% vanadium/Y_2O_3-stabilized ZrO_2 composite membrane was prepared by mechanically mixing vanadium metal powder (325 mesh, 99.5% Alfa Aesar) with Y_2O_3-stabilized ZrO_2 ceramic phase (*i.e.*, Tosoh-zirconia) and conventional PVB (Polyvinyl butyral, Sigma) as organic binder. The purpose of PVB, a common binder used in electroceramic processing, is to impart sufficient strength to the vanadium/Y_2O_3-stabilized ZrO_2 precursor mixture so that ceramic metal composite membrane will maintain its shape through pre-sintering processing procedures. The mixture was milled with acetone and ball for 1 h. The obtained powder after dry were compressed into disks of 20 mm in diameter and ca. 1.2 mm of thickness in a stainless steel mold under a hydraulic load of 8–20 ton on an area of 3.14 cm^2 by unilateral press (model 25601 series, Specac Limited, U.K.). The vanadium/Y_2O_3-stabilized ZrO_2 precursor mixtures were pre-sintered at 300 °C under helium condition for 10 h and then sintered at 1600 °C for 2 h in vacuum furnace (10^{-3}–10^{-5} Torr). The sintered disk was polished with 600 grit SiC on both surfaces by Grinder (Beta series, Buehler LTD., U.S.A.) in order to remove any potentially contaminating substances.

Helium gas-tightness tests of as-prepared membranes were conducted at room temperature with unsteady state gas permeation setup. A detailed description of the helium gas tightness test is given elsewhere [29].

2.2. Ceramic metal composite membrane characterization

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) of the metallic vanadium, Y_2O_3-stabilized ZrO_2 ceramic phase, PVB, and vanadium/Y_2O_3-stabilized ZrO_2 mixture powder was performed by Thermal Analyzer-SDT600 (TA instrument, U.S.A.) at a heating rate of 5 °C min^{-1} in helium gas and air to determine the optimum regimen of sintering.

The crystal structure of the vanadium/Y_2O_3-stabilized ZrO_2 composite membrane were characterized with an X-ray diffractometer (XRD, Rigaku Co Model D/Max 2200-Ultimaplus, Japan) using CuKα radiation in the Bragg angle range $20^\circ < 2\theta < 80^\circ$. In addition, in order to investigate the relation between reactivity and stability of ceramic metal composite membrane the vanadium metal was analyzed by high temperature XRD as a function of gas atmosphere. The morphology and composition of the dense vanadium/Y_2O_3-stabilized ZrO_2 composite membrane was ana-