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Increasing oxygen flux through a dense oxygen permeable membrane by photolithographic patterning of platinum

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Abstract

Currently attainable oxygen flux values through dense, dual conducting mixed metal oxide membranes are not yet sufficient for industrial applications, such as air separation and selective oxidation reactions. However, the addition of a catalyst near the surface of the membrane has been shown to increase the oxygen flux during gas-phase chemical reaction. This study investigated the fabrication of patterned catalyst arrays directly on the surface of dual conducting mixed metal oxide membranes and the ability to use a platinum patterned surface on the oxygen source side to increase the oxygen flux through the membrane.

Membrane processing procedures including photolithography and subsequent electron beam evaporation allowed reproducible deposition of metal arrays with specific feature sizes between 3 and 200 μm. Scanning electron microscopy and energy dispersive X-ray analysis (EDX) characterization of the membranes confirmed that the patterning process does not compromise the integrity of the membranes. The deposited catalyst arrays were stable at temperatures up to 800 °C. Placing a platinum patterned membrane surface on the oxygen source side doubled membrane oxygen flux in the temperature range studied.

Keywords: Lithography; Physical vapor deposition (PVD); Membrane; Ionic conductor; Oxygen flux

1. Introduction

The investigation of non-porous, selective oxygen permeable membranes with both ionic and electronic conductivity has received significant interest in the past decade due to the numerous applications envisioned [1–13]. Some of the possible applications of these materials include use in gas purification and oxygen separation systems [1–4] and use as reactors for the oxidation of hydrocarbons [5–11]. The transport of oxygen ions via the lattice of the non-porous materials, leads to 100% theoretical separation from nitrogen. It has even been suggested that the mobile ions can result in the presence of different active oxygen species on the membrane surface, which may increase selectivities for oxidation reactions [7,8,12].

The majority of the work reported to date has focused on modifying membrane composition or decreasing membrane thickness in order to increase oxygen flux and on improving membrane stability, especially in reducing environments [1,5,11,12]. The rate-controlling phenomena for flux include both transport through the membrane and oxygen exchange reactions at the membrane surfaces, and some studies have proposed that surface reactions are the limiting factor [2,9,11,13]. This work investigates a strategy for oxygen flux enhancement that could be used with any oxygen permeable membrane material. Depositing catalytic metal particles on the oxygen supply side (i.e., air side) membrane surface can increase membrane oxygen flux by facilitating the dissociation of molecular oxygen, and thus increasing the rate of oxygen uptake by the membrane.

Previous work has shown that it is possible to deposit spatially controlled 50 nm platinum particles onto alumina, silica, ceria and titania using electron beam lithography (EBL) followed by metal evaporation [14–18]. However, EBL would require a significant amount time to generate the large patterned areas that are being studied in this work. In order to obtain evenly distributed mono-disperse metallic clusters on the surface, contact photolithography was selected as the patterning technique for this study. While oxygen flux enhancement would be expected to increase as catalyst particle size decreases, particle size is

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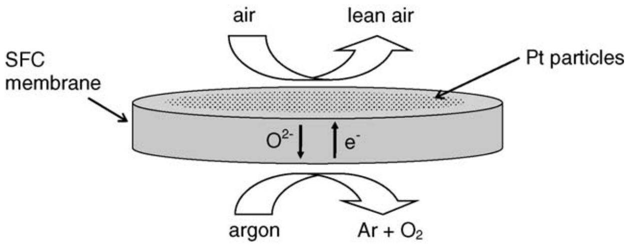

Fig. 1. Schematic of the membrane oxygen flux test environment.

not a critical factor in determining the general effect of catalyst deposition on a dense, ionic/electronic conducting ceramic membrane. Particle size optimization and subsequent scale-up deposition technique selection, while important issues, are outside the scope of this work.

After the patterning technique was selected, a procedure was developed to deposit catalytic clusters of metal on the surface of these non-porous membranes using photolithography followed by electron beam evaporation of the catalytic materials. Following successful membrane patterning, both the stability of the membrane during and after processing and the stability of the deposited catalyst pattern at temperatures up to 800 °C were assessed. Finally, a two-chambered reactor with an argon/air gradient (see Fig. 1) was used to evaluate the difference in oxygen flux results obtained using a plain membrane and a patterned membrane.

2. Experimental

The dense ceramic membranes used in this study were made by pressing 2.7 g of a non-perovskite $SrFeCo_{0.5}O_x$ (SFC) powder obtained from SCI Engineered Materials (Columbus, OH, www.superconductivecomp.com) under 1200×10^5 Pa (1200 bar) load in a 2.2 cm die. The membranes were heated in air to 1180 °C at 1.5 °C/min and held at 1180 °C for 5 h. They were then cooled to 1100 °C at 0.8 °C/min, at which time the furnace atmosphere was changed to nitrogen, and then held at 1100 °C for 48 h. Finally, the furnace was ramped down to room temperature at 1.5 °C/min.

To allow for effective photolithography, the surface of the membranes required substantial grinding and polishing. This was done on a grinding wheel starting with a 25 μm particle size aluminum oxide abrasive film and working down to 1 μm particle size. After polishing, the membranes were cleaned successively in acetone, methanol and isopropanol, and dried with a nitrogen gun. The membranes were then dehydrated in air at 110 °C for 1 h.

The photolithography and deposition process is outlined in Fig. 2. The desired bilayer photolithography process requires a lift-off resist (Microchem LOR 3B) to be spun on to the membrane surface underneath the imaging resist layer. This lift-off resist layer allows for an undercut below the imaging resist, which facilitates clean lift-off after deposition. The LOR 3B was spun on at 33.33 Hz (2000 rpm) and prebaked on a hotplate at 190 °C for 5 min. Next, a positive imaging resist (Shipley 1827) was spun on at 50 Hz (3000 rpm) and prebaked on a hotplate at 90 °C for 1 min. The coated membranes were then exposed for 1 min with the desired mask pattern on a Karl Suss MJB3 manual mask aligner and developed for about 1 min (corrected for sample variability) in a solution of 3:1 Shipley 351 developer:deionized water.

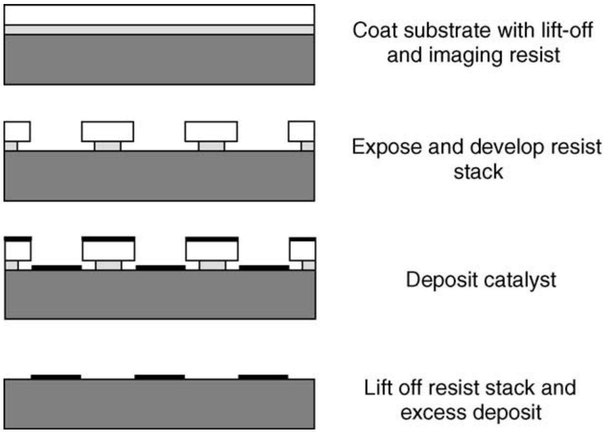

Fig. 2. Schematic outline of the bilayer lift-off processing procedure to pattern the catalyst material on the surface of the membrane.

The deposition took place in a Thermionics electron beam evaporator equipped with three 3 kW guns and an Infinicon XTC/2 deposition controller, which allowed for the specification of a desired thickness. The excess metal and photoresist on the membranes were stripped with Shipley 1165 Microposit Remover for 30 min at 70 °C and sonicated briefly in isopropanol to remove any remaining residue.

The membranes were characterized both before and after the photolithography process. Scanning electron microscopy (SEM) using a LEO 1550 field effect scanning scope was used to evaluate the effectiveness of the photolithography and deposition procedures at several different process steps. In addition, energy dispersive X-ray (EDX) analysis using the EDAX Phoenix system on the SEM was used to confirm the presence of the desired compounds in the catalyst features and also to verify that none of the processing steps altered the membrane composition. SEM images were taken at accelerating voltages ranging from 5 to 15 kV with magnifications ranging from 122× to 18.26 k×.

Pattern stability and membrane flux studies were performed using a 316 stainless steel reactor custom designed to seal a membrane between two identical hemispherical chambers of ~1 mL volume (see Fig. 1). Each chamber includes an inlet, an outlet and a sealed thermocouple, and all exposed surfaces are painted with an inert boron nitride paint to minimize the effect of the reactor material. Porter mass flow controllers maintain the gas flows into the reactor, and the effluent can be analyzed with both a Balzers Omnistar mass spectrometer and an SRI 8610C gas chromatograph. Reactor effluent flowrate is measured continuously using an Agilent ADM 2000 digital flowmeter.

For initial pattern stability testing, membranes were exposed to either oxidizing (400 °C in 20 mL/min of air) or reducing (400 °C in 20 mL/min of hydrogen) conditions for 4 h to evaluate catalyst feature stability. Flux studies were performed using air flowing at 15 mL/min as the oxygen source, and argon at