Synthesis Gas Generation Using Ionic/Electronic Oxygen Permeable Membranes

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Introduction

Using non-porous, selective oxygen permeable membranes with both ionic and electronic conductivity to provide oxygen to catalytic gas-phase partial oxidation reactions is one application of these mixed ionic/electronic conducting materials that has received significant attention [1-7]. Studies have concluded that the presence of traditional powdered partial oxidation catalysts on or near a membrane's reaction side surface can increase membrane oxygen flux by a factor of five to ten over that achievable with an inert/air oxygen gradient [1,2]. This conclusion suggests that depositing a catalyst directly on the membrane surface could increase flux even further by eliminating several transport steps and reducing local oxygen partial pressure. Previous work has shown that it is possible to deposit spatially controlled platinum particles onto alumina, silica, ceria and titania [8-12]. In order to obtain arrays of evenly distributed mono-disperse metallic particles in a relatively short time, contact photolithography was selected as the patterning technique for this work, but the general results should be transferable to any patterning/deposition process.

This study reports the effect of catalyst particle deposition on membrane oxygen flux when the catalyst is located on the oxygen supply side of a membrane. Preliminary results for enhanced powdered catalyst stability ascribed to decreased carbon deposition in the presence of the evolved membrane oxygen are also presented. Finally, pattern and membrane stability under oxidizing, reducing, and reaction conditions is discussed.

Experimental

The membranes used in this study were made by pressing non-perovskite $SrFeCo_{0.5}O_x$ (SFC) powder under a 1200 bar load. The green disks were sintered in air at 1180 °C for 5 hours followed by 48 hours in nitrogen at 1100 °C. Membrane surfaces to be patterned were polished with successively smaller aluminum oxide abrasives to allow reproducible photolithography of 3 μm features. After polishing, membranes were cleaned and then dried in air at 110 °C for 1 hour.

Catalyst particle patterning and deposition followed conventional semiconductor processing methodology for bilayer photolithography and electron beam evaporation. Multi-component cluster patterns of support oxide and metal were also produced by repeating the entire photolithography and deposition process for the second material after careful alignment of the second photomask pattern on top of the deposited pattern. Membranes were characterized before and after the photolithography process using a scanning electron microscope (SEM) with an integrated energy dispersive x-ray (EDX) analyzer that was used to verify that none of the processing steps altered the membrane composition and to confirm the presence of the desired compounds in the deposited features.

Pattern stability, flux, and reaction studies were performed using a two-chambered 316 stainless steel reactor designed to seal a membrane between its two identical hemispherical chambers of ~1 mL volume. Each chamber includes an inlet, an outlet, and a sealed thermocouple, and all exposed surfaces are painted with an inert BN_3 paint to minimize the effect of the reactor material. Reactor effluent composition was analyzed by both continuous mass spectrometry and intermittent gas chromatography, and effluent flowrate was monitored continuously.

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 H_2) conditions for four hours to evaluate catalyst feature stability. Flux studies were performed using air flowing at 15 mL/min as the oxygen source and argon at 20 mL/min as the sweep gas. Steady state mole fractions of Ar, N_2, and O_2 in the sweep gas effluent were determined from mass spectrometer data at 50 °C intervals up to 800 °C, and any leakage through the gold ring gasket seals was quantified using the N_2 mole fraction and the known inlet and outlet flowrates. CO_2 reforming reaction studies were performed at 700 °C or 750 °C using a 20 mL/min feed of equal parts carbon dioxide and methane.

Results and Discussion

Deposition of Catalytic Materials

Due to its relatively low cost, nickel was chosen as the initial test material for the deposition process. Nickel catalyst features were successfully patterned on unpolished membrane surfaces in sizes ranging from 100 µm to 20 µm with a thickness of approximately 30 nm. This initial testing demonstrated the necessity of machine polishing of the membranes to reproducibly obtain features smaller than 20 µm.

Platinum was patterned reproducibly on polished membranes with feature sizes ranging from 100 µm to 2 µm. Figure 1 shows an SEM image of 3 µm disks of platinum patterned on a membrane surface with a deposition thickness of 60 nm.

Cerium oxide was also patterned on a polished membrane surface with the same range of feature sizes as platinum. Although CeO_2 sublimes rather than melting like the metals tested previously, EDX verified that the deposited particles contained the same relative amounts of cerium and oxygen as the starting material. After successful deposition of the oxide particles, multi-component catalyst clusters were patterned on a membrane surface in the form of 3 µm diameter platinum disks supported on 5 µm diameter CeO_2 disks.

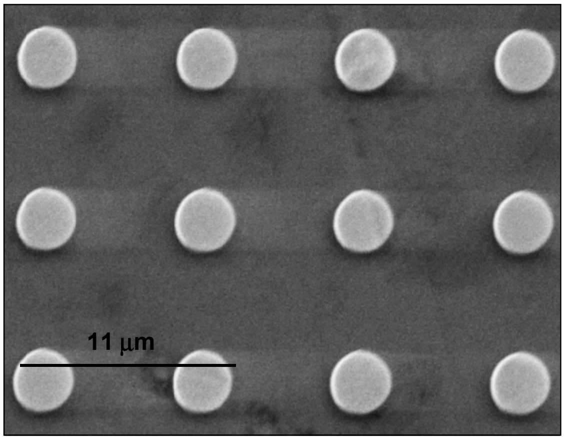

Figure 1: SEM image of 3 µm Pt features on SFC membrane surface.

Stability of Patterns in Oxidizing and Reducing Environments

Nickel and oxide patterned membranes with feature sizes ranging from 15 to 200 µm were exposed to the 400°C oxidizing and reducing environments described in the

Experimental section. No migration of the metal or the oxide deposits across the surface of the membrane was observed on any sample. The pattern stability and the stability of the SFC membrane material in higher temperature reducing environments with elevated amounts of water are discussed below.

Effect of Patterning on Membrane Oxygen Flux

Oxygen flux was determined at temperatures between 500 and 800 °C for both unpatterned polished membranes and identical membranes patterned with 5-micron diameter platinum circles spaced by 3 microns. The patterned membrane surface was installed on the oxygen source side of the two-chambered reactor, and fluxes were determined at each temperature of interest from stabilized mass spectrometer data.

As shown in Figure 2, the membrane patterned with platinum exhibited roughly twice the oxygen flux as the unpatterned membrane at temperatures between 600 °C and 800 °C. In addition to the increase in flux, the deposited platinum pattern also reduced the minimum temperature at which detectable oxygen flux occurred from 600 °C for the plain membrane to 550 °C for the patterned membrane. The plain membrane fluxes in Figure 2 are consistent with values in the literature [1,13]; the patterned membrane results do not take into account the reduction in SFC surface area caused by the patterning.

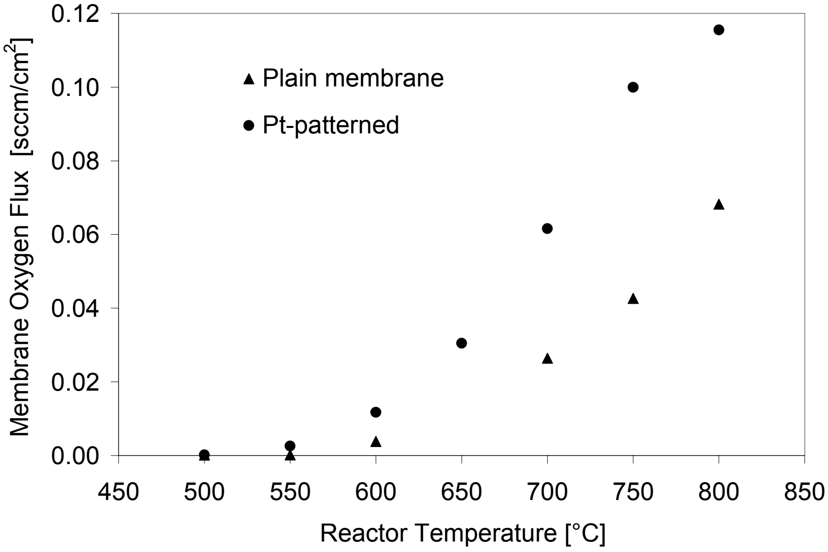

Figure 2: Oxygen flux as a function of temperature for unpatterned and Pt-patterned membranes under an air/argon gradient

Membrane Effect on Reforming Catalyst Performance

Initial catalytic reaction studies were performed at 750 °C with a conventional powdered Pt/ZrO_2 catalyst (0.5 wt% Pt) on both an SFC membrane and a BN_3 coated stainless steel disk (a “blank” membrane). Although conversion was initially lower over the SFC membrane than over the blank, the membrane-supported catalyst showed stable conversion over the observed time period while the blank-supported catalyst’s activity dropped steadily from its initial high point and was lower than that of the SFC supported catalyst after two hours. The lower initial conversion is believed to result from incomplete pre-reaction catalyst reduction caused by membrane oxygen flux during reduction.

In tests without powdered catalyst, a patterned membrane that had been reduced at the reaction temperature showed higher initial activity at 750 °C than both the unreduced patterned membrane and the plain membrane, which behaved identically. Conversions for all three cases converged to similar low values after 4 hours.

Membrane Material Stability under Reforming Reaction Conditions

One advantage of the disk membrane configuration over a tubular membrane is the ability to analyze the membrane's reaction side surface with SEM and EDX following a reaction study. After exposure to the CO_2 reforming mixture at 700 °C for 4 hours, thin nickel features (10 nm) became undetectable by SEM even though the membrane material appeared to be otherwise unchanged. Interestingly, an EDX surface scan confirmed that the nickel was still present in its original pattern, which indicates its possible incorporation into the membrane material itself.

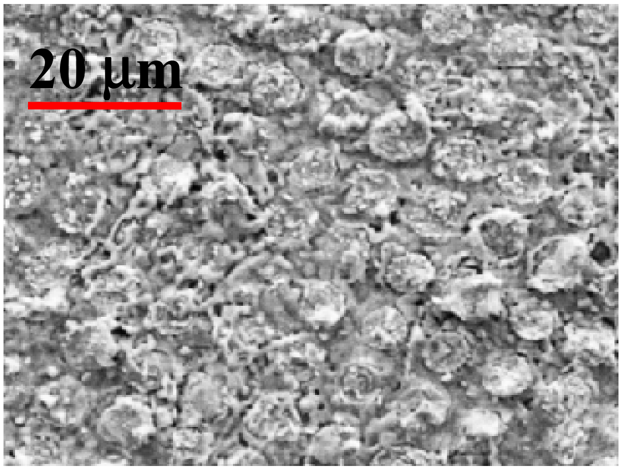

Figure 3: SEM image of Pt-patterned membrane surface after reduction and CO_2 reforming of CH_4 at 750°C for 11 hours.

CO_2 reforming reaction studies performed on platinum patterned membranes at 750 °C showed significantly different results. Figure 3 depicts a surface patterned with 5 μm Pt particles after an extended exposure to higher temperature environments, including an oxygen flux study between 500 °C and 800 °C that was followed by reduction at 750°C in hydrogen and CO_2 reforming of methane at 750°C for 11 hours. It seems obvious that a significant restructuring of the membrane surface has occurred, although it is still possible to see the outlines of the Pt features. EDX characterization of the surface revealed that the platinum is still present and that the outgrowths consist mainly of iron and cobalt oxides. This suggests a segregation of iron and cobalt from the $SrFeCo_{0.5}O_x$ structure under this high temperature reducing environment.

Other experiments were conducted without the water-producing reduction step to examine the possibility that the surface reconstruction was a result of the higher water levels generated during reduction. These runs produced similar results, however, as did a CO_2 reforming run with an unpatterned membrane, indicating that neither water nor the deposited catalyst is individually responsible for these apparent surface phase transitions. Attempts to clarify the basis of this surface reconstruction are ongoing and include investigations into the combined effect of membrane sintering conditions and subsequent test environment on membrane phase stability.

Conclusions

This study developed the methodology required to deposit catalytic materials in a spatially controlled manner on a functional mixed metal oxide membrane and then evaluated the effect of the patterned catalyst on membrane performance. The membrane material was unaffected by the patterning process, and the deposited catalyst patterns were shown to be stable when subjected to both oxidizing and reducing environments at 400 °C. However, higher temperature environments were observed to have the potential to cause restructuring of the SFC membrane material, which can reduce patterned catalyst exposure and possibly affect membrane properties as well. Powdered catalyst activity was successfully stabilized by the presence of the membrane during CO_2 reforming of methane, although complete catalyst reduction may be hindered by the membrane's oxygen production. Finally, it was demonstrated that a platinum pattern deposited on the oxygen source side of a membrane significantly increases oxygen flux through the membrane by facilitating membrane oxygen uptake. Ongoing investigations are focusing on the aforementioned membrane restructuring phenomenon as well as on the effect on oxygen flux of other metals/metal oxide systems such as palladium, silver, and the Pt/CeO_2 multi-component catalyst particles.

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