HYDROGEN TRANSPORT CATALYTIC MEMBRANE REACTORS

Anthony F. Sammells, Michael V. Mundschau, Richard Mackay, and Shane E. Roark
Eltron Research Inc.
4600 Nautilus Court South
Boulder, CO 80301
www.eltronresearch.com

Introduction
Eltron Research Inc. is developing low cost, multi-phase membranes for separating hydrogen from hydrogen containing feedstreams. This is being addressed using material composites which facilitate high proton and electron conduction. Membranes are being developed for high (>750°C) and low (<425°C) temperature applications and have been successfully operated under a high pressure differential (250 psi) for extended times. Under ambient pressure, hydrogen transport rates >25mL/cm²/min have been achieved at 400°C.

Experimental
Doped perovskites \( \text{A}_{1-x}\text{B}_{x}\text{B}'_{1-y}\text{B}'_y\text{O}_3-\delta \), where \( x \) and \( y \) are the fractions of dopants in the A and B sites, respectively, and \( \delta \) is the number of oxygen vacancies,\(^{1,2}\) were prepared using conventional high temperature solid state synthesis techniques. Corresponding cermets \( \text{A}_{1-x}\text{B}'_{x}\text{B}_1\text{B}'_y\text{O}_3/M \) were prepared by sequential pressing and sintering at elevated temperatures under controlled atmosphere conditions.

The inlet hydrogen source was initially diluted with helium. This facilitated determination of the membrane seal quality. \( \text{H}_2 \) and \( \text{He} \) fractions within inlet and sweep streams were determined by TCD-GC using a Shimadzu GC 14-A with a 12-ft. by 1/8-in. stainless steel Carbosphere column. Ultra-high purity Ar was used as the carrier gas to optimize detection limits for hydrogen and helium.

Results and Discussion
Cermet membranes under development at Eltron consist of a proton conducting ceramic phase and a low cost hydrogen permeable metallic phase. Figure 2 shows an SEM image of a cermet membrane.

![SEM image of a cermet membrane containing 46 wt.\% metal phase. The proton-conducting ceramic appears as the light regions and the metal phase as the dark regions.](image.png)

Hydrogen flux, \( J \), through dense mixed proton/electron conducting membranes in the absence of surface kinetic limitations is dependent on the membrane thickness, \( t \), according to,

\[
J = \frac{\sigma_{\text{bulk}}E}{t}
\]

where \( E \) is the Nernst potential. Figure 3 contains a plot of theoretical hydrogen transport rates versus membrane thickness.

Several approaches currently are being pursued at Eltron for fabrication of thin film hydrogen separation membranes. The most straightforward strategy is to deposit a thin layer of dense membrane material on a porous support of the same composition. The challenge for this approach is to match the shrinkage rates of the support and thin film to enable sintering without membrane cracking. Shrinkage of the thin film was controlled by varying the surface area of the powder prior to sintering, whereas, shrinkage of the support was controlled by adjusting the material porosity. Using this strategy, the shrinkage mismatch between the thin film and support was...
minimized to a only a few percent, and homogenous crack-free thin films approximately 100 µm thick routinely are prepared. An example is shown in the SEM image in Figure 4.

Figure 4. SEM image showing a cross section of a 100 µm thick dense membrane deposited onto a porous support of the same composition.

Hydrogen separation membranes have been operated at 250 psi pressure differential between the hydrogen feed and sweep side at elevated temperatures continuously for >1000 hrs. The performance of our low cost membranes operating under ambient pressure conditions as a function of temperature (Figure 5) and Ar sweep rate (Figure 6) on the hydrogen permeate side are shown below. As can be seen, hydrogen diffusion fluxes >25 mL/cm²/min have been achieved at 400°C.

A simplified block diagram of a hydrogen separation unit installed in an integrated gasification combined cycle (IGCC) plant is shown in Figure 7. The diagram shows three options for installation, indicated as baseline, alternative 1, and alternative 2. The alternative 1 option assumes the membrane materials will be tolerant to sulfur and particulate material, and that the raw syngas from coal gasification can be sent directly to the unit. The baseline option also assumes sulfur tolerance, but the gas stream must be filtered prior to entering the unit. If the membrane materials are not sulfur tolerant, then alternative 2 will be necessary, and the unit will be inserted after desulfurization. This condition will require reheating the gas stream through a heat exchange prior to entering the hydrogen separation unit.

Figure 5. Hydrogen diffusion as a function of operating temperature under ambient pressure conditions. Ar sweep rate on permeate side 300 mL/min.

Figure 6. Hydrogen diffusion as a function of Ar sweep rate on the permeate side at 400°C. Ambient pressure conditions.

Figure 7. Diagram of an IGCC plant with three installation options for a hydrogen separation unit.

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References