Directionally Dependent Transport in a Mixed Ionic-Electronic Conducting Membrane for Separating Oxygen from Air

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Surface exchange and bulk diffusion processes resist ionic oxygen transport in mixed ionic-electronic conducting (MIEC) perovskite membranes. In regimes of mixed resistance, the outwards ionic flow rate per unit length from a tube to the shell (F^{out}) is predicted to exceed that from the shell to the tube (F^{in}) under the same partial pressure difference. Numerical simulations for typical parameter values predict enhancement factors (F^{out} / F^{in}) of about 1.05. The directional dependence is not encountered when either the surface exchange or bulk diffusion are the controlling resistance. Experimental data are in qualitative agreement with theoretical results. Enhancement factors between 1.14 and 1.59 were observed in tubes at 1000°C with $\rho = 1.61$ (where $\rho = r_2/r_1$) fabricated from $La_{0.5}Sr_{0.5}Fe_{0.8}Ga_{0.2}O_{3-\delta}$ (LSFG).

Introduction

Ionic transport of oxygen through MIEC's is limited by two transport mechanisms: surface exchange and bulk diffusion of oxygen [1-8]. Chemical instability and mechanical constraints on membrane thickness limit our ability to increase the oxygen flux by reducing the bulk resistance. Kim et al [9] developed a model for radial oxygen flow through tubular MIEC membranes. They assumed that the bulk diffusion coefficient is constant and that the molar concentration of ions in the membrane is constant. When both resistances are present, their model predicts that the flow rate satisfies the relation

$$\frac{F}{\alpha}\ln\rho = \ln\left[\frac{\sqrt{\frac{P^2}{P_0}} - \frac{F}{r_2\beta}}{\sqrt{\frac{P^1}{P_0}} + \frac{F}{r_1\beta}}\right] \qquad (1)$$

where F is the ionic flow of oxygen per unit length [mol/(sec*cm)], r_2 and r_1 are the outer and inner tube radii, respectively [cm], P^2 and P^1 are the partial pressure of oxygen at r_2 and r_1, respectively, P_0 is at 1 atmosphere and

$$\beta = \pi k_{io} c_i \quad ; \quad \alpha = \pi D_a c_i \quad ; \quad D_a = D_i\sigma_e/(\sigma_e+\sigma_i) \qquad (2)$$

k_{io} being the surface exchange constant [cm/sec], and c_i being the average molar concentration of oxygen ions in the solid [mols ions/cm^3], D_a being the bulk ambipolar diffusion coefficient [cm^2/sec], D_i the ionic diffusion coefficient, σ_e the electronic conductivity, and σ_i the ionic conductivity.

The ratio between the bulk diffusion resistance and the surface exchange limitation is related by the characteristic length, L_{Do}. The limiting resistance in a real system is also a function of the membrane thickness. A new dimensionless parameter called the *characteristic resistance* is defined as

$$M = \frac{L_{Do}}{(r_2 - r_1)} = \frac{D_a/(r_2 - r_1)}{k_{io}} = \frac{\alpha/(r_2 - r_1)}{\beta}. \qquad (3)$$

When M >> 1, the surface exchange is the limiting transport mechanism. Conversely when M

<< 1, the bulk diffusion is the controlling mechanism. When the ionic transport is limited by both transport mechanisms, M is of order unity.

Prediction of flow dependence on direction and simulations

The numerator of the rhs of Eqn (1) describes the potential difference at the high oxygen partial pressure side of the membrane. The denominator describes the low pressure side. In order to simplify the equations, we define the high and low side oxygen partial pressure as P^h and P^l and denote

$$\left(\frac{P^h}{P_0}\right)_{num} = p^h \qquad \left(\frac{P^l}{P_0}\right)_{denom} = p^l \tag{4}$$

The inwards flow (F_{in}=F>0) occurs when the high partial pressure is at r_2. In this case Eqn (1) becomes

$$\frac{F^{in}}{\alpha}\ln\rho = \ln\left[\frac{\sqrt{p^h} - \frac{F^{in}}{r_2\beta}}{\sqrt{p^l} + \frac{F^{in}}{r_1\beta}}\right] \tag{5}$$

An outwards flow (F_{out}=-F) occurs when p^h is at r_1. In this case Eqn (1) becomes

$$\frac{F^{out}}{\alpha}\ln\rho = -\ln\left[\frac{\sqrt{p^h} + \frac{F^{out}}{r_1\beta}}{\sqrt{p^l} - \frac{F^{out}}{r_2\beta}}\right] \tag{6}$$

After eliminating the natural logs from each side, equating $\sqrt{p^h}\beta$ in these two equations, and manipulating algebraically, we get

$$F^{in}\left[1+\left(\frac{1}{\rho}\right)^{F^{in}/\alpha+1}\right] + \sqrt{p^l}\,\beta\, r_1\left[1-\left(\frac{1}{\rho}\right)^{(F^{in}+F^{out})/\alpha}\right] = -F^{out}\left[\left(\frac{1}{\rho}\right)^{F^{in}/\alpha} + \left(\frac{1}{\rho}\right)^{F^{in}/\alpha}\left(\frac{1}{\rho}\right)^{F^{out}/\alpha}\right] \tag{7}$$

The term in the bracket multiplying F^{in} on the lhs of (7) is larger than the term multiplying $-F^{out}$ on the rhs of (7) since

$$1 > \left(\frac{1}{\rho}\right)^{F^{in}/\alpha}$$

$$\left(\frac{1}{\rho}\right)^{F^{in}/\alpha+1} > \left(\frac{1}{\rho}\right)^{F^{in}/\alpha+1}\left(\frac{1}{\rho}\right)^{F^{out}/\alpha} \tag{8}$$

Moreover, the second term on the lhs of (7) is positive as $\left(\frac{1}{\rho}\right)$< 1. It then follows that

$$\left|-F^{out}\right| > F^{in} > 0$$

We conclude that the outwards ionic flow of oxygen will exceed the inflow at the same high and lean partial pressures. We define an *enhancement factor*, E, to be the ratio between the two flows ($\left|-F^{out}\right|/F^{in}$). The enhancement factor depends on the relative tube radii, the high

and lean partial pressures, and the characteristic resistance. A directional flow dependence does not exist in the following cases:

1. When the surface exchange is rapid relative to the bulk diffusion.
2. When bulk diffusion is rapid relative to the surface exchange.
3. When the transport is through a slab membrane, i.e., $\rho = 1$.

Numerical simulations were conducted to determine the expected magnitude of the directional dependence using typical parameter values reported in the literature when necessary. The values of F^{in} and F^{out} were computed from Eqns (5) and (6) using Microsoft Excel.

Numerical simulations show that the enhancement factor is strongly dependent on the ratio ρ, but not on the magnitudes of either r_2 or r_1. As the characteristic resistance approaches zero, the bulk diffusion limitations dominate the total resistance and the directional enhancement disappears. As the characteristic resistance approaches infinity, surface exchange limitations dominate and the directional enhancement again disappears. The maximum enhancement in the case of $\rho = 2$, $p^h = 0.200$, and $p^l = 0.002$ is about 16% and occurs for M slightly less than 0.1.

The enhancement factor is sensitive to the value of ρ, and the magnitude of the enhancement factor increases with increasing values of ρ for any given value of the characteristic resistance. Moreover, the maximum value of the enhancement factor increases as the value of ρ increases. The characteristic resistance at which the maximum enhancement factor occurs depends on the operating pressure.

In an experimental study it is rather easy to investigate the impact of the partial pressure of the oxygen on both sides of the membrane on the ionic flow. Simulations predict that the enhancement factor is a monotonic decreasing function of the lean oxygen side partial pressure. On the other hand, the enhancement factor attains a local maximum at some intermediate value of the concentrated oxygen side partial pressure.

The simulations indicate that there is a definite advantage in designing membrane reactors with outwards flow of oxygen, as it increases the flow with no change in the equipment or operating costs. Simulations predict especially high enhancement under conditions that exist for ~1.0 cm thick LSFG membranes operating at 1000°C in the presence of the partial oxidation of methane reaction. A typical enhancement value of 1.14 is predicted in these conditions.

Experimental study of flow directional dependence

We conducted experiments to check the validity of the predicted flow directional dependence and its magnitude. A membrane tube was constructed from LSFG powder obtained from Praxair Specialty Ceramics (Woodinville, WA). The powder and mold were pressed at 40 kpsi in a cold isostatic press (CIP). The pressed green powder was fired in air at 1335°C for 2 hours using heating/cooling rates of 75°C/hr.

Oxygen and nitrogen were mixed to form the oxygen rich feed. Helium and oxygen were mixed for the lean feed. The total gas flow rates in the oxygen rich and oxygen lean

mixtures were ~ 210 mL/min. and ~350–370 mL/min., respectively. A higher flow rate of helium was used to minimize the lean side oxygen partial pressure change due to the ionic transport. Four independent 4-way valves controlled the sampling and switching of the two feeds.

The gas streams' compositions were determined by a Varian Micro-Gas Chromatograph model 4900. The compositions of all the process streams could be sampled in this system. Oxygen and nitrogen were separated using a 10-meter molecular sieve column with He carrier. Detection of the gas species was made on a thermal conductivity detector. The gas composition was determined at better than 0.1% accuracy at total oxygen levels from 0.1%-100% and 1% accuracy for total oxygen levels of 0.01% - 0.1%. The minimum level of detection is 10ppm and the minimum quantifiable amount (at least 10% accuracy) is 100ppm.

The characteristic resistance of the membrane was estimated to be about unity so that the flow is limited by both diffusion and the surface exchange rate. The experiments were conducted at 1000°C and a total pressure of 1.2 atm. The oxygen mole fractions of oxygen in the rich mixtures were 0.10, 0.20, and 0.30 (p^h = 0.12, 0.24 and 0.36 respectively). The mole fractions of oxygen in the lean mixtures were 0.000, 0.015 and 0.045 (p^l = 0.000, 0.018, and 0.054, respectively).

In all the experiments the oxygen flow exhibited directional dependence and the enhancement factor exceeded unity. The observed enhancement factors were between 1.14 and 1.59 depending on the operating pressures. Data for p^l= 0.000 and 0.018 show an increase in the enhancement as the oxygen concentrate partial pressure increases in the range tested. Data are also collected at p^l=0.054 which further confirmed the enhancement. The data qualitatively verified the theoretical predictions: Increasing the oxygen partial pressure on the concentrated side increased the ionic flow; Decreasing the oxygen partial pressure on the lean side increased the ionic flow; and F^{out} was greater than F^{in} in all the experiments. It is apparent that the experimental ionic flow was higher than that predicted by the model. In several cases the difference was a factor of over five.

The data collected at p^l= 0.018 and 0.054 are important from a qualitative perspective, because they show that the enhancement is observed even when there is a finite partial pressure of oxygen on the lean side of the membrane. Comparison of the simulated and experimental results reveals that the simulation substantially under-predicted the observed enhancement in all the experiments. The experiments verified the prediction that the enhancement will be larger as the concentrate side partial pressure increases. However, the observed magnitude of increase differed from the predicted one. The direction of the predicted impact of the lean side partial pressure of oxygen on the enhancement factor differed from the observed one. The observed enhancement factors decreased as the lean side pressure of oxygen decreased, while the theory predicted the inverse trend.

The disparities between the experimental data and the theoretical predictions are most likely due to the simplifying assumptions used in the model. Specifically, the assumption of constant ionic concentrations inside the membrane and its surfaces may be an oversimplification. More general transport equations have been proposed [4,10] to address this, but there is still no developed method for experimentally probing the local ionic concentrations at the surfaces of the membranes.

Conclusions

The simulations of the model and experiments reveal that the outwards oxygen flow rate through a tubular membrane exceeds that of the inwards flow when both diffusion and surface exchange resistance limit the transport. The magnitude of this enhancement is predicted to depend on the pressures of operation, the membrane dimensions, and the characteristic resistance parameter M. The simulation predicted enhancement factors in the range of 1.05 – 1.10 under typical operating conditions. The experiments verified the model prediction that the outwards flow rate exceeds the inwards flow. However, the experimentally determined enhancement factors of 1.14 – 1.59 are much higher than those predicted theoretically. The discrepancy between the theoretical prediction and experimental data are probably due to some invalid assumptions made in the derivation of the model. The experiments suggest that designers of membrane reactors should exploit this directional enhancement. Further experimental and theoretical studies should be conducted to determine the cause for the deviations between the model and experiments and to enable a reliable and accurate prediction of the enhancement.

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