Oxygen Flux Increases Through MIEC Membranes by Enhanced Surface Exchange

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Introduction

The mixed ionic-electronic conductor (MIEC) $La_xSr_{(1-x)}Fe_yGa_{(1-y)}O_{3-\delta}$ (LSFG) has good oxygen transport characteristics[1,2] and is stable at high-temperatures in the presence of methane.[3] The oxygen flux through LSFG under an air/helium gradient is of the order of 0.1 ml O_2/min cm^2 at 974°C.[2] To be economically competitive in a syn-gas process the minimum oxygen flux through an MIEC membrane is 5–10 ml/(cm^2 min).[4]

The oxygen flux through an MIEC membrane is affected by both surface exchange and bulk diffusion processes. Model analysis and experiments indicate that under mixed transport control the outwards flux exceeds the inwards flux through a bare MIEC tube[5,6] when the surface exchange coefficient, ambipolar bulk diffusion coefficient, and oxygen concentration in the ionic lattice are constant and pressure independent. The outwards and inwards fluxes are equal in the limit of a single limiting resistance, either surface exchange or bulk diffusion. Gerdes and Luss[6] predicted that when the surface exchange coefficients, k_{io}, on the interior and exterior tube surfaces are different, a higher oxygen flux will be obtained when the surface with the larger surface exchange coefficient is exposed to the oxygen lean stream.

The surface exchange resistance of a membrane may be decreased by surface modification.[6,7] Murphy et al.[7] first reported an increase in the oxygen flux by addition of a sparse Pt layer on a disk membrane at temperatures ranging from 600–800°C. We report here novel data about the impact of a sparse platinum surface layer on the oxygen flux through a MIEC tubular membrane and its directional dependence.

Results

The details of the experimental apparatus and the procedure of preparing the membrane tubes are described elsewhere.[5] Experiments were performed on bare and layered membrane tubes at 1000°C. Air was fed to the oxygen-rich side and the dimensionless oxygen rich partial pressure ($p^h = P_i/P_0$) was raised by increasing the operating pressure. The lean feed stream was 99.999% helium flowing at approximately 200 sccm/min and 122 kPa. Experiments were conducted using a MIEC with a 5–10 Å thick Pt surface layer that was photolithographically deposited by the research group of Susan Stagg–Williams at the University of Kansas. The Pt surface coverage was sparse and noncontinuous. The reported flux data are based on the interior area of the tubular membranes.

The oxygen flux through a bare LSFG tube at 1000°C with air on the oxygen rich side and helium sweeping the lean side is used as a performance baseline. The corresponding outwards and inwards flux were 0.29 and 0.22 ml O_2/min cm^2, respectively. This inwards flux is comparable with the ~0.10 ml O_2/min cm^2 reported by Kim et al.[1] at a temperature of 974°C on a LSFG tubular membrane of similar dimensions. The factor of 2.2 difference between the two independently recorded measurements is acceptable considering that flux differences of factors of 10 and more have been reported for other apparently identical membranes. The maximum recorded nitrogen leakage in any experiment was smaller than 0.010 ml N_2/(min cm^2) at 340 kPa, corresponding to an O_2 leak smaller than 0.6% of the total O_2 flux rate.

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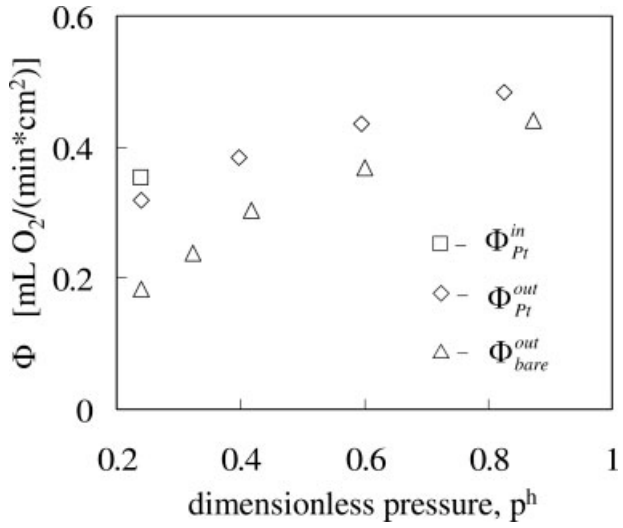

Figure 1. Dependence of oxygen flux rate on p^h for LSFG tube coated with a 5–10 Å thick layer of Pt (◇, Φ^{out}_{Pt}); □, Φ^{in}_{Pt} and for a bare tube (△, Φ^{out}_{bare}). Temperature is 1000°C.

Figure 1 depicts experimental oxygen flux data for both the bare LSFG membrane and the membrane with a sparse Pt exterior surface layer. The oxygen flux increased as the dimensionless oxygen-rich potential increased. Φ^{out} and Φ^{in} of the coated tube exceeded that of Φ^{out} through a bare LSFG tube operating under the same potential gradient by 70 and 90%, respectively. The difference in the flux between bare and nanolayered Pt tubes diminishes with increases in the dimensionless oxygen rich pressure, p^h. The 70% outward flux increase at $p^h = 0.24$ decreases to an interpolated value of 18% at $p^h = 0.60$. However, the oxygen flux through the Pt coated membrane exceeded that of the bare one for all feed potentials tested.

The inwards flux for the Pt-coated membrane exceeded the outwards flux. For example, at $p^h = 0.24$, Φ^{out} and Φ^{in} were 0.32 and 0.35 ml O_2/min cm^2, respectively. This directional dependence was confirmed by repeated experiments, and is the inverse of that observed for the bare tube. Furthermore, the increase in the oxygen flux was larger when the Pt coating was exposed to the oxygen rich gas, which is the inverse of previous theoretical analysis of a surface exchange enhanced tube.[6]

Experiments were conducted to determine the oxygen flux at 1000°C through a LSFG membrane on the exterior surface of which a ~110-μm thick Pt layer was coated. These experiments were conducted using LSFG prepared in-house and a He/CO_2 mixture as the sweep gas. The micro-Pt layer coating decreased the outwards oxygen flux by 6.5% with $p^h = 0.24$ and a 1–20% decrease is measured at five other values of p^h in the range of 0.12–1.20. Only one experiment at p^h of 0.06 resulted in a flux increase (10%).

Discussion

The increase in the oxygen flux upon the deposition of a sparse Pt layer indicates that its presence decreases the surface exchange resistance. The relative increase in the oxygen flux is in good agreement with observations by Murphy et al.[7] The deposition of the Pt had a surprising impact on the directional dependence of the flux through the tubular membrane, which resulted in $\Phi^{in} \geq \Phi^{out}$. All previous analysis predicted that the outwards oxygen flux exceeds that of the inwards one, especially when the lean gas is exposed to the surface with a greater surface exchange coefficient.[5,6] Although there exists a small parameter space in the layered membrane model[6] for which $\Phi^{in} \geq \Phi^{out}$ can be predicted, the experiments reported here are conducted within a parameter range for which $\Phi^{in} \geq \Phi^{out}$ is not possible. We believe that the sparse platinum layer changed either the surface exchange mechanism and/or the surface reaction kinetics. Interestingly, when the membrane was coated with a thick continuous Pt layer $\Phi^{in} \leq \Phi^{out}$ as predicted by the model.

The oxygen flux through the membrane coated with a relatively thick Pt layer was smaller than that through the bare membrane. In contrast, coating the membrane with a sparse platinum layer nearly doubled the oxygen flux under some conditions. The decrease in the oxygen flux for the thick Pt layer indicates that the impact of the decreased surface resistance on the flux was smaller than the combined increase in the diffusional resistance through the Pt and the resistance at the Pt-membrane interface. It may also indicate that MIEC surface sites required for the oxygen exchange are blocked by the Pt layer, which does not conduct oxygen ions.

The fact that a surface sparsely populated with Pt led to a higher flux than the bare MIEC suggests that a triple phase consisting of (Pt)/(MIEC surface)/(oxygen gas) is involved in the exchange process. Several different mechanisms may explain the role of Pt in incorporating oxygen from the gas phase into the ionic lattice. Explanations include:

i Pt facilitates the transfer of electrons from $O_{2(ads)}$ on the MIEC surface;
ii O^{2-} is produced at a MIEC surface site, and Pt stabilizes O^{2-};
iii Pt aides the adsorption of O_2(g), and catalyzes its dissociation to O^{2-}.

To explain these effects consider the reaction sequence (written in Kroger–Vink notation),

$$O_2 + S_{(s)} \leftrightarrow O_{2(ads,MIEC)} \tag{1}$$

$$O_{2(ads,MIEC)} + 4e^- \leftrightarrow 2O^{2-}_{(ads,MIEC)} \tag{2}$$

$$2O^{2-}_{(ads,MIEC)} + V_o^{\cdot\cdot} \leftrightarrow O_o^{\times} \tag{3}$$

where S_s is adsorptive surface site, $V_o^{\cdot\cdot}$ is an oxygen vacancy, and $O_o^{\times}$ is an oxygen ion on the oxygen lattice. The first and second effects may be explained by reactions (1) and (2), respectively.

The third effect may be due to either the reaction sequence

$$O_2 + Pt_{(s)} \leftrightarrow O_{2(ads,Pt)} \tag{4}$$

$$O_{2(ads,Pt)} + 4e^- \leftrightarrow 2O^{2-}_{(ads,Pt)} \tag{5a}$$

$$2O^{2-}_{(ads,Pt)} + V_o^{\cdot\cdot} \leftrightarrow O_o^{\times} \tag{6a}$$

or the reactions,

$$O_2 + Pt_{(s)} \leftrightarrow O_{2(\text{ads,Pt})} \quad (4)$$

$$O_{2(\text{ads,Pt})} + 4e^- \leftrightarrow 2O^{2-}_{(\text{ads,MIEC})} \quad (5b)$$

$$2O^{2-}_{(\text{ads,MIEC})} + V^{\cdot\cdot}_{\text{o}} \leftrightarrow O^{\times}_{\text{o}} \quad (6b)$$

where $Pt_{(s)}$ is a Pt surface site. In reaction sequence (4) through (6a), it is hypothesized that Pt transfers the O^{2-} directly to an oxygen surface vacancy, i.e., the participating MIEC surface specie is an oxygen vacancy. In reaction sequence (4) through (6b), surface migration of O^{2-} occurs from Pt to some MIEC site. Here, the triple phase is replaced by a series of oxygen surface transfer steps.

The basic proposed mechanisms are not intended to fully describe the entire set of possible reaction steps. The surface exchange mechanism for a bare MIEC has only recently been narrowed to a small set of likely steps, with many questions remaining.[8] For example, the adsorbed oxygen specie(s) could be any of the group O^{2-}, $2O^-$, O_2 and may or may not share some charge with the bulk surface. Likewise, the single limiting step could be adsorption of oxygen, oxygen dissociation, or incorporation of oxygen. Once the surface exchange mechanism on the bare MIEC tube is more reliably known, the role of Pt may be clarified.

Conclusions

Adding a sparse Pt layer to the surface can increase the oxygen flux because of an enhancement of the surface exchange. A photo-lithographical deposition of a platinum surface layer on the order of 5–10 Å thick enhanced the ionic flux through the membrane by more than 90% in some cases. The sparse platinum layer inverted the model predicted directional dependence in the tubular membrane so that $\Phi^{\text{in}} > \Phi^{\text{out}}$. On the other hand, deposition of a micro-layer of Pt did not increase the oxygen flux but also did not invert the predicted directional dependence.

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