Coupling of dielectric barrier discharge plasma with oxygen permeable membrane for highly efficient low-temperature permeation

Qiankun Zheng\textsuperscript{a,1}, Yaqiong Xie\textsuperscript{a,1}, Jinkun Tan\textsuperscript{a}, Zhi Xu\textsuperscript{a}, Ping Luo\textsuperscript{a}, Tianlei Wang\textsuperscript{a}, Zhengkun Liu\textsuperscript{a}, Feng Liu\textsuperscript{b}, Kui Zhang\textsuperscript{b}, Zhi Fang\textsuperscript{b}, Guangru Zhang\textsuperscript{a,4}, Wanqin Jin\textsuperscript{a}

\textsuperscript{a} State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, 30 Puzhu Road(S), Nanjing, 211816, PR China
\textsuperscript{b} College of Electrical Engineering and Control Science, Nanjing Tech University, 30 Puzhu Road(S), Nanjing, 211816, China
\textsuperscript{1} School of Chemical Engineering and Advanced Materials, Newcastle University, Newcastle Upon Tyne, NE1 7RU, UK

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\textbf{A B S T R A C T}

Ceramic oxygen permeable membranes (OPMs) are widely considered the “next generation” technology for pure oxygen separation and catalytic membrane reactors. However, the main issue of OPM is high operating temperature (above 800 °C) and resulting implications for materials, cost, as well as operating complexities (e.g., sealing, creep deformation, and thermal shock during thermal cycling). A new design for coupling OPM $\text{La}_0.6\text{Sr}_0.4\text{CoO}_3\text{Fe}_0.5\text{O}_3.3$ with a dielectric barrier discharge plasma (a type of atmospheric pressure non-thermal plasma) is proposed for highly efficient low-temperature (600 °C) oxygen permeation. This study demonstrates that the plasma can activate the surface exchange reactions. Applying 15 W air-plasma can effectively reduce the apparent activation energy of the permeation process from 136.6 to 43.1 kJ mol$^{-1}$. The oxygen flux is increased by a factor of nearly 30 at 600 °C with a plasma power of 15 W. The newly developed plasma-membrane micro-reactor design enables further performance enhancement at lower operating temperatures and integration with solid oxide fuel cells, catalytic membrane reactors, and oxygen permeable membranes.

1. Introduction

Oxygen permeable membranes (OPMs) attract significant attention because of their high potential for oxygen separation and energy conversion applications \cite{1,2}. Considered a transformative technology, OPMs were developed for high-purity oxygen production, and a 100 ton/day air separation unit was recently constructed by Air Products in the USA \cite{3}. However, cost and long-term durability remain great challenges for the more extensive commercialization of OPMs. The key issue limiting their development is high operating temperature. The typical operating temperatures of the current state of the art OPMs are 800–1000 °C; this provides important advantages including high oxygen flux, highly efficient integration with combustion processes \cite{4}, and high catalytic activity and reaction kinetics in catalytic membrane reactors (CMRs), e.g., partial oxidation of methane \cite{5–9}, methane coupling \cite{10–12}, methane aromatization \cite{13,14}, hydrogen production by water splitting \cite{15,16}, decompositions of carbon dioxide \cite{17,18} and nitrogen oxides \cite{19–21}. However, high operating temperatures also result in high system costs, and high performance-degradation rates. Other problems include slow start-up and shutdown cycles. Additionally, high-temperature creep deformation, thermal shock, cation segregation, and failure of sealing are fatal for these brittle ceramic OPMs. Low-temperature OPMs can effectively solve the above problems and have the potential to reduce costs by using low-cost materials and interconnects for the balance of plants.

After decades of development, significant progress has been achieved in material development. Perovskite oxides (ABO$_3$) exhibit mixed ionic and electronic conducting ability, and are the most extensively studied OPM materials. Various perovskites for OPMs have been investigated, among which strontium-containing and cobalt-containing perovskite oxides (e.g., Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3.6}$ \cite{22–25} and La$_{0.6}$Sr$_{0.4}$Co$_{0.5}$Fe$_{0.5}$O$_{3.3}$ \cite{26–28}, which are the most studied OPM materials) are particularly attractive because of their high mixed

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\textsuperscript{1} Corresponding author. State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, 30 Puzhu South Road, Nanjing, 211816, PR China.

E-mail address: Guangru.Zhang@njtech.edu.cn (G. Zhang).

\textsuperscript{1} Qiankun Zheng and Yaqiong Xie contributed equally.

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conductivity and permeability. However, high conductivity comes at the cost of low chemical stability, including cation segregation, and demixing under the reducing environment in CMRs [5,6,8]. Considerable efforts have also been directed at developing asymmetric supported structures (including asymmetric membranes [22,28–30] and hollow fiber membranes [6,9,11,20,26,31]), which allow a significantly thinner dense separation layer and allow the reduction of the operating temperature.

OPMs are dense and gas-tight. Oxygen ions can only migrate through the membrane because the direct permeation of oxygen molecules is blocked. The permeation process (Fig. 1a) includes (1) the dissociation and ionization of oxygen occurring at the membrane surface of the feed side, (2) simultaneous bulk-diffusion of oxygen ions and electron/electron holes in the bulk phase, and (3) recombination of oxygen ions to form oxygen molecules at the membrane surface of the permeate side [32,33]. The overall efficiency depends on the surface exchange reaction and bulk diffusion. They are normally considered the two most significant processes for OPMs. In general, the bulk phase diffusion is the rate-determining step (slow kinetics) at high temperatures, whereas the surface exchange becomes the rate-determining step at lower temperatures and it decomposes into highly reactive atomic O and molecular O2 [41]. Therefore, the chemistry in oxygen plasma is mainly driven by electrical field/energetic electrons, and the ROSs generated via excitation, dissociation, ionization, etc., differ from those in the thermal and catalytic activation processes [42,43].

In this study, we propose a new design for coupling DBD plasma with OPMs (DBD-membrane micro-reactors). The ROSs from oxygen plasma are expected to promote the surface exchange reaction, and thus, the overall permeation at relatively low temperature (<750 °C). The electrodes of DBD plasma are modified to be compliant with our membrane system. A disk-like La0.6Sr0.4Co0.2Fe0.8O3−δ (LSCF) membrane is selected because of its slower surface exchange kinetics, which can demonstrate plasma enhancement on the surface reaction. In this new membrane system, the effects of plasma on the membrane surface exchange and overall oxygen permeation are systematically investigated in the range of 600–900 °C. The effects of plasma power on gas-phase composition, surface microstructure, and phase structure are also investigated in detail. Preliminary insights on the plasma enhancement of OPMs are given: it can be used to design other integrated processes to enhance the gas-surface exchange, such as in CMRs, solid oxide fuel cells, and other gas permeation processes (either at high or low temperatures).

2. Experimental

2.1. Powder preparation

The La0.6Sr0.4Co0.2Fe0.8O3−δ (LSCF) oxides were prepared by a solid-state synthesis method. La2O3, SrCO3, Co2O3, and Fe2O3 were mixed with ethanol according to stoichiometry in a high-energy ball mill (450 rpm for 8 h) (Retsch, PM100, Germany). The mixed powders were dried.

Fig. 1. Oxygen permeation process in a mixed conducting oxygen permeable membrane and a DBD-membrane micro-reactor. (a) Classic oxygen permeation involving surface exchanges and bulk diffusion at high temperature driven by a differential oxygen partial pressure (Pf > Pp); (b) oxygen permeation involving oxygen-plasma at the feed side. Reactive oxygen species (ROSs) were generated in the DBD. (Its structure and luminous images were shown.)
at 60 °C and then sieved (100 meshes). The powders were calcined at 950 °C for 5 h to obtain the prepared LSCF oxide. The heating and cooling rate were 2 °C min⁻¹. All the chemicals with purities higher than 99.5% were purchased from Sinopharm, China.

2.2. Membrane preparation

After mixing the pre-calcined mixture with absolute ethanol, a high-energy ball mill was used for mixing for 4 h (rotating speed 450 rpm), and subsequently the mixed slurry was dried at 60 °C for 12 h. Green disk-like membranes were prepared by an uniaxially press at 400 MPa. Dense membranes were obtained by sintering at 1290 °C for 5 h in static air. The heating and cooling rate was 2 °C min⁻¹. The density of the LSCF membrane was determined by Archimedes Principle, which is 6.147 g cm⁻³. Theoretical density was calculated to be 6.348 g cm⁻³ from XRD. The relative density of the membranes was about 96.83%.

2.3. Characterization

The X-ray diffraction (XRD, Bruker, model D8 advance, Germany) with Cu Kα radiation in the range of 20° ≤ 2θ ≤ 80° was used to observe the crystal phase structures. The morphologies of the disk-like membrane were obtained using a scanning electron microscope (SEM, Hitachi S-4800, Japan) equipped with an energy dispersive X-ray spectrometer (EDX) detector. The optical emission spectra emitted from the discharge were obtained through a spectrometer (Ocean optics, FLAME-T-UV-VIS-ES, United States, 200–850 nm range, 1.5 nm resolution).

2.4. Oxygen penetration measurement

A DBD-LSCF micro-reactor as Fig. 2 was used to conduct the oxygen permeation experiments. The disk-like membrane was sealed on a dense corundum (alumina) tube by a silver sealant. A programmable temperature controller (HF-Kejing, OTF-1200X, China) was used to control the temperature of the samples. The sealed disk-like membrane was heated to 930 °C and hold for 1 h, and then organics were removed and the metal silver was softened to achieve a gas-tight sealing. The leakage level was measured before the permeation. Experiments start only when the leakage level is less than 1%. Mass flow controllers (Sevenstar, CS200, China) were used to adjust the gas flow rates.

The oxygen permeation flux was calculated below:

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J_{O_2} = \left( \frac{C_{O_2}}{C_{N_2}/4.02} \right) \frac{Q}{S}
\]

2.5. DBD-membrane micro-reactor

The electrodes of DBD plasma were modified to be compliant with the disk-like membrane system. Figs. 1b and 2 show the configuration of the DBD-LSCF micro-reactor. A mesh electrode (width and height are 38.0 mm and 30.0 mm, respectively) is closely attached to the outmost surface of the corundum (alumina) tube while the other wire electrode (diameter of 1 mm) are located in the tube centre. Both the electrodes are made of stainless steel 316 L (Fig. S1). The corundum tube is acted as a dielectric barrier layer with inner and outer diameters of 8.0 mm and 12.0 mm, respectively, while leaving a 3.5 mm discharge gap. The oxygen plasma takes place in the discharge gap between the overlapping area of the mesh and wire electrodes. A high-frequency (9 kHz) and high-voltage AC sinusoidal power supply (Suman, CTP-2000K, China) were equipped. The high voltage signal was measured by a high-voltage

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![Fig. 2. Schematic diagram of the DBD-LSCF micro-reactor (L refers to the direct distance between the electrode and the membrane).](image-url)
probe (Tek P6015). The discharge current was obtained by a non-inductive resistance of 50 Ohm resistor. Fig. 1b shows the luminous images of the plasma micro-reactor. The pink-purplish glow is distributed on the outmost surface and inside the discharge gap of the ceramic tube.

3. Results and discussion

3.1. Oxygen permeation measurement under different gas components

The effects of DBD plasma on membrane permeation are investigated. The LSCF symmetrical dense membrane (1 mm thickness) is mounted on top of the corundum tube near the DBD side. Fig. 3a shows the temperature- and plasma power-dependent oxygen permeation in the DBD-LSCF micro-reactor with air as the oxygen source. The plasma power dissipated into the micro-reactor was obtained by the integration of the voltage versus current signals recorded by an oscilloscope (Fig. S2). The oxygen permeation fluxes of bare LSCF and the DBD-LSCF membranes increase with temperature. This is mainly attributed to the temperature effect on the enhancement of the lattice vibration and oxygen diffusion rates [32, 33]. By applying plasma with low power consumption (from 5 to 15 W), extraordinary enhancement of oxygen permeation flux is observed. As shown in Fig. S3a, introducing the air-plasma can effectively reduce the apparent activation energy of the permeation process from 136.6 to 43.1 kJ mol$^{-1}$ when the plasma power is increased from 0 to 15 W. The apparent activation energies include the activation energy of surface exchange and oxygen migration in the bulk. The migration activation energy is the barrier that oxygen must surmount to migrate through the rigid crystal lattice: it is calculated by minimization of the total lattice energy and is the intrinsic property of a material [32], which is not likely to be affected by plasma. A tentative conclusion can therefore be drawn that the plasma mainly acts on membrane surface exchange and serves to decrease the activation energy of surface exchanges. The phenomena are commonly observed in other plasma-catalyst systems where the plasma enhances the catalyst surface reaction and lowers the reaction activation energy. In this case, the higher plasma power and higher concentration of ROSs further enhance the surface exchange reaction, resulting in a higher oxygen flux (Fig. 3a).

At lower temperature, the surface exchange becomes the rate-determining step. Therefore, the effects of plasma at low temperature are expected to be more significant than those at high temperatures. As shown in Fig. 3b, the enhancement effects of the air-plasma on the oxygen permeation process are particularly evident at low temperatures (600–700 °C). Comparing to the LSCF membrane without plasma at 600 °C, applying only 15 W air-plasma can increase the oxygen permeation flux by a factor of nearly 30.

Oxygen permeation behavior is also evaluated in the oxygen/argon mixed gas (21% O$_2$, 79% Ar) plasma. As shown in Fig. 3c, the oxygen/argon-plasma promotes oxygen permeability. A higher plasma power results in a higher oxygen flux. However, the apparent activation energy barely changes with the introduction of the oxygen/argon mixture (Fig. S3b). The application of 20 W plasma increases the oxygen flux only by the factor of 2 at 600 °C (Fig. 3d). This is mainly because

![Fig. 3. The oxygen permeation performance of the DBD-LSCF micro-reactor. (a)&(c) Oxygen permeability in the DBD-LSCF micro-reactor with air-plasma and oxygen/argon-plasma, respectively; (b)&(d) the enhancement (R) of oxygen permeation flux by plasma at different temperature with air-plasma and oxygen/argon-plasma, respectively. R = (F$_{O_2}$, plasma – F$_{O_2}$, LSCF)/F$_{O_2}$, LSCF × 100%, where F$_{O_2}$, plasma and F$_{O_2}$, LSCF are the oxygen permeation fluxes with plasma and without plasma, respectively. (F$_{purge}$ gas = 90 ml min$^{-1}$, F$_{feed}$ gas = 30 ml min$^{-1}$).]
nitrogen is more effective than argon in promoting the formation of ROSs \cite{44}, and hence, the oxygen flux. Meanwhile, the enhancement by oxygen/argon plasma on oxygen permeation flux is not stable and shows fluctuations. (R values increase with operating temperature until 800 °C). This may be caused by the unstable discharge of argon plasma at high temperatures. As shown in Fig. S2, the oxygen-argon plasma exhibits a characteristic of breakdown at 900 °C, where the gas gap loses its electrical insulation and becomes a conductive channel, resulting in an unstable plasma \cite{45}.

The differences in the excitation energy, dissociation energy, and bond energy of the gases that may be involved in the experiment are compared in Table S1. Although the apparent gas temperature is low, the electron temperature can be up to 10,000–100,000 K (1–10 eV) in a DBD plasma. Highly energetic electrons are sufficient to activate inert molecules into reactive species, including radicals, excited atoms, molecules, and ions \cite{46}. According to the Maxwellian electron energy distribution function (EEDF) versus electron energy, the electrons in the high energy tail of the EEDF can contribute to the activation of oxygen molecules for ROS formation. In Fig. S4a&b, the emission spectra of O (\(^3\)p\(^5\)p) at 777 nm can be detected in both air-plasma and oxygen/argon-plasma \cite{47–49}. However, O (\(^3\)p\(^5\)p) is mainly produced by direct electron impact dissociation excitation, considering the small number of O\(_2\) molecules and O atoms. Therefore, it yields a weaker O emission, whereas strong emissions are observed for nitrogen (at 300–500 nm) and argon (higher than 700 nm). The excitation energy for nitrogen is 6.1 eV; therefore, in DBD plasma, a large number of metastable groups are generated \cite{50}. These excited nitrogen molecules in plasma may collide with oxygen molecules for enhanced ROSs formation (possible reactions involving nitrogen, argon, and oxygen in plasma are shown in Table S2 \cite{51–53}). However, they also inevitably produce nitrogen oxides. In this study, 100–500 ppm nitrogen oxides are detected at the feed side of the micro-reactor. The O emission intensity (777 nm) is not adequate for a quantitative analysis. However, with the increase in air-plasma power, the O (777 nm) emission intensity increases qualitatively (Fig. S4c), which was not observed in oxygen/argon-plasma (Fig. S4d). These phenomena may correspond to the variation in oxygen permeation flux under different plasma atmospheres and power conditions.

### 3.2. Effects of operation and architecture on the performance

As shown in Fig. 4a, as the applied voltage of the air plasma
increases, the plasma discharge efficiency, power, and oxygen permeation flux increase until 13 kV, and then decrease. Normally, the applied voltage is closely related to the discharge characteristics of plasma. The transition of the discharge regime and discharge characteristics (voltage, current, and heat effect) are shown in Fig. S5 and Movie S1. A low applied voltage (below 12 kV), discharge occurs on the surface of the electrode and the corundum gap, showing the characteristics of uniform glow discharge (and later filamentary discharge), and a discharge characteristic of high voltage-low current. At an applied voltage higher than 13 kV, arc discharge occurs and the discharge characteristic is high voltage-high current. In this case, the plasma is transformed from non-thermal plasma (a DBD plasma with electron temperature higher than gas temperature) to thermal equilibrium plasma (an arc plasma with electron temperature similar to gas temperature), and a significant drop in discharge efficiency is observed. Notable, these characteristics are acquired near room-temperature. There is a certain deviation in the high-temperature micro-reactor. However, the relationship between plasma voltage and discharge characteristics is illustrated qualitatively, and demonstrating that low voltage and uniform discharge are the key factors for achieving high oxygen ionization efficiency and oxygen permeation flux.

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In addition to the gas components, the effects of the flow rate of the feed stream and sweep stream, and the position of the DBD discharge electrodes to the membrane on the discharge characteristics and oxygen permeability were evaluated. The flow rates of streams have been recognized to contribute to the kinetics of the surface exchange, and particularly, affect the O\textsubscript{2} partial pressure at the boundary layer close to the membrane surface [54]. A higher flow rate is beneficial for creating a maximum O\textsubscript{2} partial pressure gradient and results in a higher oxygen flux. These effects can be observed in Fig. 4b with an increase in the flow rate of either the feed stream or purge stream. As shown in Fig. S4c&d, the change in the flow velocity barely affects the intensity of the ROSs generated by the air-plasma or oxygen/argon-plasma, which proves the validity of the above conclusion.

ROSs are formed in the discharge area between the electrodes. However, any particles generated in plasma interact with other particles through the collision process. The momentum, kinetic energy, potential energy, and charge are exchanged between particles through collision, which results in recombination after the ROSs leave the discharge area [55]. Therefore, the distance between the electrode and the membrane directly determines the amount of ROSs that reach the membrane. As shown in Fig. 4c, as the distance between the discharge electrode and the membrane increases, the oxygen permeation flux sharply decreases. This is mainly because of the long distance, which increases the chances of recombination of ROSs and reduces the number of ROSs reaching the membrane surface. Apparently, reducing the distance between the electrodes and membrane is the key to effective improvement of the membrane flux. However, the perovskite LSCF membrane is a mixed conductor with the ability of electronic conduction. With the decrease in the distance, the possibility of breakdown (creating arcs) between the electrode and the membrane increases.

3.3. Membrane morphology and phase structure

A Comparison of the surface SEM micrographs of the membrane before and after the air-plasma experiments (Fig. 5a&b), shows that the
membrane surface undergoes serious structural changes. The clear grain boundary structure on the fresh membrane surface completely disappears after the air-plasma experiment, whereas a few micropores appear on the surfaces. The element distribution (Fig. 5c) and phase structure (Fig. 5d) of the membrane surface also changed significantly. A small amount of Ag and Al can be observed on the membrane surface after plasma exposure because of the sputtering of Ag and Al from silver sealant and corundum in plasma, respectively. The XRD patterns of the membrane surface show that after the experiment, the intensity of diffraction peaks of LSCF significantly decreases, and a small amount of SrFeO$_3$ forms on the membrane surface. The excessive energy plasma particles “knock off” molecules from the sample surface, causing damage (including physical and atomic level defects) and forming impurities on membrane surface. The damage also be confirmed by a significant decrease in the intensity of the diffraction peaks of the membrane after air-plasma exposure. Plasma (such as argon-plasma) is widely used for generating abundant oxygen vacancies because oxygen and neutral atoms can be dissociated using high-energy ions on oxide surface [56,57]. However, a shift of the diffraction peak of the membrane towards a higher diffraction angle after air-plasma exposure is observed (Fig. 5d). This may be attributed to the decrease in cell parameters caused by oxidation by the large number of ROSs in the air-plasma.

In addition, we investigate the evolution of the microstructure of the membrane surface and bulk at different plasma exposure times (2 and 5 h) and voltages (2 and 10 kV). As shown in Fig. 5e, the surface structure of the membrane is more seriously damaged with the increase in exposure time at the same voltage or with the increase in voltage at the same exposure time. Pore structures caused by physical damage observed on the membrane exposed to 2 kV plasma for 5 h, whereas the pores are covered by impurities with the increase in voltage to 10 kV. The cross-sectional morphology and element distribution of the membrane after the air-plasma experiment (exposed to 10 kV plasma for 5 h) are studied (Fig. 5f). Micropores are barely noticeable on the cross-section whereas a uniform distribution of elements is observed. Such a strong interaction affects the outermost surface of the membrane more than the morphology or composition of the bulk membrane, indicating that the DBD-membrane micro-reactor can remain stable in long-term oxygen separation.

4. Conclusions

A novel DBD-membrane system that demonstrates a significant enhancement of low-temperature oxygen permeation in ceramic OPMs is designed. The ROSs from oxygen-plasma mainly lower the surface exchanges and enhance the reaction kinetics. A very small plasma power output (below 20 W) can effectively improve the oxygen permeation flux at low temperatures. At 600 °C and 15-W plasma power, the oxygen permeation flux of the disk LSCF membrane increases by a factor of nearly 30. The low power consumption of plasma allows the use of low-power electricity, such as solar and wind. The results also demonstrate that the gas composition (air-plasma and oxygen/argon-plasma), flow rates of feed gas and purge gas, and position of the DBD discharge electrodes with respect to the membrane have a significant effect on the discharge characteristics, generation of ROSs, and thus, oxygen permeation flux. The use of high oxygen flux materials, advanced membrane structure (e.g. asymmetric or hollow fiber membranes), or other types of atmospheric pressure plasma (e.g. microwave plasma, radio frequency glow discharge or plasma jets) has great potential to further improve the flux. This technology has not fully matured yet, meaning that significant advances are still possible. This study offers new opportunities for developing OPMs and CMRs with an enhanced surface exchange at much lower temperatures.

CRediT authorship contribution statement


Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References
