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# Surface oxygen vacancy and oxygen permeation flux limits of perovskite ion transport membranes

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## ABSTRACT

The mechanisms and quantitative models for how oxygen is separated from air using ion transport membranes (ITMs) are not well understood, largely due to the experimental complexity for determining surface exchange reactions at extreme temperatures ( $> 800$  °C). This is especially true when fuels are present at the permeate surface. For both inert and reactive (fuels) operations, solid-state oxygen surface vacancies ( $\delta$ ) are ultimately responsible for driving the oxygen flux,  $J_{O_2}$ . In the inert case, the value of  $\delta$  at either surface is a function of the local  $P_{O_2}$  and temperature, whilst the magnitude of  $\delta$  dictates both the  $J_{O_2}$  and the inherent stability of the material. In this study values of  $\delta$  are presented based on experimental measurements under inert ( $CO_2$ ) sweep: using a permeation flux model and local  $P_{O_2}$  measurements, collected by means of a local gas-sampling probe in our large-scale reactor, we can determine  $\delta$  directly. The ITM assessed was  $La_{0.9}Ca_{0.1}FeO_{3-\delta}$  (LCF); the relative resistances to  $J_{O_2}$  were quantified using the pre-defined permeation flux model and local  $P_{O_2}$  values. Across a temperature range from 825 °C to 1056 °C,  $\delta$  was found to vary from 0.007 to 0.029 ( $< 1\%$ ), safely within material stability limits, whilst the permeate surface exchange resistance dominates. An inert  $J_{O_2}$  limit was identified owing to a maximum sweep surface  $\delta$ ,  $\delta_{max}^{inert}$ . The physical presence of  $\delta_{max}^{inert}$  is attributed to a rate limiting step shift from desorption to associative electron transfer steps on the sweep surface as  $P_{O_2}$  is reduced. Permeate surface exchange limitations under non-reactive conditions suggest that reactive (fuel) operation is necessary to accelerate surface chemistry for future work, to reduce flux resistance and push  $\delta_{past}$   $\delta_{max}^{inert}$  in a stable manner.

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## 1. Introduction

The global need for pure oxygen for use in energy applications including fuel synthesis and conversion processes is expanding rapidly [1]. This is driven in part by increasing emphasis on clean combustion and carbon capture and storage (CCS) technologies, highlighted as being critical to bringing  $CO_2$  levels back into check [2]. Oxygen ion transport membranes, ITMs, allow for 'passive' separation of oxygen from air at high temperatures, offering the potential for reducing the energy penalty associated with traditional cryogenic air separation units [3]. The high temperature operating requirement of ITMs makes them most effective when integrated in the same module for fuel combustion/synthesis. Significant oxygen flux performance gains are realized due to the presence of fuel, which further increases their appeal [4].

The challenge to bring this promising separation technology into practice lies in designing cost-effective, energy efficient ITM modules. For this, representative oxygen flux mechanisms need to be specified,

in the presence of both inert gases and fuels; providing tools with which separation or reactive module designs can be optimized. High-level studies have already determined the lower limit for oxygen flux required to achieve economic viability of 10 ml/cm<sup>2</sup> min or 7  $\mu$ mol/cm<sup>2</sup> s [5]. The question still remains however how this can be attained in practice.

The findings presented in this study relate to the inert experimental characterization of the oxygen flux and associated model for the perovskite ITM  $La_{0.9}Ca_{0.1}FeO_{3-\delta}$  (LCF) as detailed in [6]. The LCF composition pursued in this work has been found to be, while not optimum for flux performance, very resilient against breaking down in reducing (fuel) environments, as demonstrated by the work in [7]. The oxygen flux resistances, attributed to gas-phase/solid-state surface exchange resistances and solid-state bulk diffusion, are quantified to identify the critical processes as oxygen passes across the ITM. Experimental measurements provide unique insight into the oxygen lattice deficiency, or the oxygen vacancy, at both the oxygen-rich and oxygen-lean surfaces; this defines the solid-state oxygen flux driving potential. Ultimately, by determining the surface oxygen vacancy concentrations, the oxygen flux model can be made universal for both inert gas and fuel (reactive) environments, a critical step towards the development of this fundamental understanding. Our

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large-scale experimental ITM reactor, built specifically to probe the gases near the permeate membrane surface, was first introduced in [8] with adaptations detailed in [6].

The oxygen flux model, proposed in [9], re-examined and tested in [6] for inert operation, is shown in the following equation:

$$J_{O_2} = \frac{D_V k_f (P_{O_2}^{0.5} - P_{O_2}^{\prime 0.5})}{2t_m k_f (P_{O_2}^{\prime 0.5} P_{O_2}^{\prime\prime 0.5}) + D_V (P_{O_2}^{0.5} + P_{O_2}^{\prime 0.5})} \quad (1)$$

Here  $D_V$  is the solid-state oxygen vacancy diffusion coefficient, a parameter which through the vacancy conductivity (given by the Nernst–Einstein relation) defines the oxygen flux driven by a chemical potential gradient as specified by the Wagner equation for mixed ionic–electronic conductors [10].  $D_V$  for LCF has been determined in a separate study using transient dilatometry methods [11]; this value is in good agreement with previous  $D_V$  studies [12]. In relation to the solid-state diffusion resistance, the membrane thickness  $t_m$  is further required. The driving chemical potential gradient in Eq. (1) is specified by the local (taken at the ITM surface) gas phase measurements, termed  $P_{O_2}$  and  $P_{O_2}^{\prime}$  for the high- and low-oxygen surfaces respectively. The  $k_f$  and  $k_r$  terms in Eq. (1) define the gas-phase to solid-state surface exchange reactions, in this case assumed to be single-step, pseudo-zero-order reactions as in [6].

It should be noted that a distinct assumption is made with regard to the surface exchange reactions at the high- and low-oxygen surfaces: the forward and reverse reaction rates,  $k_f$  and  $k_r$ , are identical. This avoids excessive parameter fitting and ensures for a compact permeation flux expression as in Eq. (1). In reality the different environments between the surfaces, air versus  $CO_2$ , may interact differently with the surface, particularly occupying/blocking oxygen vacancy sites. This would require extensive datasets with more rigorous parameter fitting: however it turns out that the air surface exchange resistance is negligible (see Section 3), meaning the fitted values of  $k_f$  and  $k_r$  most accurately describe the surface exchange reactions at the permeate/ $CO_2$  surface.

In general, surface exchange reactions, particularly in the presence of fuel, are less straight-forward to quantify: large amounts of temperature-dependent data for Arrhenius fitting of parameters are required. The introduction of gaseous fuels can react with oxygen in both the homogeneous gas and heterogeneous surface phases. This high level of complexity in the surface exchange reactions, particularly upon the introduction of fuels into ITM modules, makes it far more difficult to reliably build quantitative flux models.

The solid-state diffusion of oxygen ions (or oxygen vacancies) across an ITM is reasonably well understood, as shown in Eq. (2); this diffusion as related to the concentration of oxygen vacancies  $C_V$  at either surface can thus be used as the basis for a ‘universal’ oxygen flux model. As a recap double- and single-primes relate to the low (or sweep) and high feed (or air) surfaces respectively, whilst  $D_V$  is assumed to be independent of  $C_V$ : this is reasonable given the low values of  $C_V$  expected and observed in this work:

$$J_{O_2} = \frac{D_V}{2t_m} (C_V^{\prime\prime} - C_V^{\prime}) \quad (2)$$

Using the solid-state flux Eq. (2) as a basis, valuable (albeit indirect) insight into the heterogeneous surface exchange reactions will be possible for any range of fuel/inert gas compositions. This study applies this method to new inert-based data presented here, with future studies to focus on the reactive case when fuels are introduced at the permeate side of the membrane.

Throughout this paper, the inert experimental conditions (detailed in [6] and summarized next) are such that the oxygen-rich ITM side is fed by air, termed the air side, whilst the oxygen-lean surface is fed by  $CO_2$ , termed the sweep side.

**Table 1**

Experimentally determined values for the surface exchange reactions in inert conditions using the zero order inert flux model (Eq. (1)).

Material constant	Pre-exponential factor (A)		Activation energy ( $E_A$ ; J/mol)
	Units	Value	
$k_f$	cm/atm <sup>0.5</sup> s	1.013	$7.810 \times 10^4$
$k_r$	mol/cm <sup>2</sup> s	$2.010 \times 10^{-3}$	$1.106 \times 10^5$
$D_V$	cm <sup>2</sup> /s	$4.980 \times 10^{-3}$	$5.960 \times 10^4$

## 2. Oxygen flux measurements

Further testing of our ITM reactor, following significant upgrades as detailed in [6], determined that safe operation up to 1100 °C was possible. Subsequently several datasets (46 datapoints total) were collected in the temperature range 825–1056 °C, with two ITM thicknesses (0.95 and 1.50 mm) and for a range of  $CO_2$  sweep flow rates (1000–2000 standard cubic cm/min, sccm). This data was collected with a consistent, non-flux-limiting air side flow rate of 6000 sccm. The inert flux model, the parameters of which are shown in Table 1 were fitted using these 46 datapoints.

The experimental protocol to collect this data was strictly adhered to for all measurements: our large scale ITM reactor was heated up to temperature, and air and  $CO_2$  flows applied to the air and sweep sides respectively, using the same procedure to that outlined in [6]. Measurement of gas concentrations was again carried out using an Agilent 490 Micro-gas chromatograph (GC). Multiple gas sampling points were available on the reactor, distinguishing between local and bulk measurements. The oxygen flux was characterized by comparing the well-mixed or bulk measurements at both the inlet and outlet of the reactor, whilst local gas conditions at the sweep surface were collected and analyzed using the same quartz probe shown in [6]. For the new high temperature dataset, temperatures were incrementally increased and the reactor allowed to stabilize for 30 min minimum, before multiple (at least six) gas samples were drawn and measured from both bulk and local sample points. The oxygen flux calculation using the bulk measurements is detailed next.

To calculate the oxygen flux,  $J_{O_2}$ , under inert conditions a mass balance was applied between the inlet and outlet gas streams, ensuring conservation of atomic species C and O ( $N_2$  was used to monitor and track the finite air leak). The change between the mass flow in,  $m_{in}$ , and mass flow out,  $m_{out}$ , allowed for calculation of the mass flow rate due to oxygen flux,  $m_{jO_2}$ , which could then simply be converted to  $J_{O_2}$  in  $\mu\text{mol}/\text{cm}^2 \text{ s}$  after subtracting the leak. The volumetric flow rate in,  $\dot{V}_{in}$ , was known and the volumetric flow rate out,  $\dot{V}_{out}$ , was left as an unknown.  $CO_2$  was assumed to not dissociate under these conditions: this was confirmed through the absence of any CO as measured by the GC. Using the C mass balance, Eq. (3) (where ideal gas assumptions and the molar weight of C  $M_C$  are included), with 100%  $CO_2$  flow at the inlet,  $\dot{V}_{out}$  could duly be determined as per Eq. (4). The mol fractions of species are termed  $X_k$  (as measured by the GC), where  $k$  is either  $O_2$ ,  $N_2$  or  $CO_2$ :

$$\dot{V}_{in} \frac{PM_C}{RT} = \dot{V}_{out} \frac{PM_C}{RT} X_{CO_2out} \quad (3)$$

$$\dot{V}_{out} = \frac{\dot{V}_{in}}{X_{CO_2out}} \quad (4)$$

With  $\dot{V}_{in}$  and  $\dot{V}_{out}$  known,  $m_{in}$ ,  $m_{out}$  and  $m_{AirLeak}$  (mass flow attributed to the air leak, tracked by the outlet  $X_{N_2}$  measurement) can be calculated as per the following equations:

$$m_{in} = \dot{V}_{in} \frac{PM_{CO_2}}{RT} \quad (5)$$

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