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Current Opinion in Chemical Engineering

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Abstract

Here we provide an overview of recent developments in high-temperature electroceramic oxides for the transport of gas-phase species via dual ion conductivity. The electroceramic oxide is used in the form of a dense membrane when it exhibits ionic conductivity for two distinct ions and as a porous host matrix supporting a guest liquid-phase ion conductor when it supplies a path for a single ion, the path for the other being supplied by the liquid phase. We focus on water transport and carbon dioxide transport in single and dual phase membranes respectively.

1. Introduction.

Ion-conducting dense ceramic membranes exhibit very high selectivities as the membrane material can be tailored to exhibit significant mobility and diffusivity for individual species. High temperature oxygen permeable membranes, usually operating at 500°C and higher, function through an oxygen-ion flux which is matched by an equal and opposite (in charge terms) electron flux; ion transfer is almost exclusively due to the point defect oxygen-ion vacancy mobility. The transport mechanism in such a mixed ionic electronic conducting (MIEC) phase is represented in Figure 1. The notation for point defects in a crystal lattice is given in Kröger-Vink notation [1] where $V_O^{\bullet\bullet}$ represents a vacancy at a site in the oxygen sublattice with a net +2 charge and e' represents an electronic defect. Examples of Kröger-Vink notation with explanation are provided in Table 1 for illustration.

Figure 1

Table 1

These MIECs, often based on ABO_3 perovskite-type mixed metal oxides, are currently under intensive investigation for their oxygen transport properties for a number of industrially important applications where controlled and distributed supply of pure oxygen is of benefit. Some perovskite materials, most notably those based on $BaCeO_3$, can also demonstrate protonic and electronic conductivity resulting in hydrogen permeable materials. Hydrogen can react with lattice oxygen forming hydroxyl groups:

The hydrogen associated with the hydroxyl group is mobile and can hop, in the form, of a proton, to a neighbouring lattice oxygen. The proton migrates between lattice O_o^x sites as an interstitial defect, $H_i^\bullet$, and is effectively a transition state:

Investigation of the required properties to demonstrate hydrogen permeation is still in progress. Observation indicates the importance of (i) high molar volume (large lattice constants) achieved by incorporation of large A-site cations such as Ba^{2+} (ii) high crystal symmetry, as close to cubic as possible and (iii) a metal-oxygen bond strength that facilitates mobility of the protons. The ΔG of formation of the mixed oxide and the propensity to form hydroxyl groups are also key factors. There is no single, universal explanation for this conductivity but a number of useful reviews dealing in depth with this topic exist [2-4].

Most of the high temperature, ion transport work reported thus far has been centred on single phase oxides where one of the charge carriers is electronic. The extensive body of literature on MIEC work is not the focus of this contribution, instead we direct the reader to a number of recent reviews [5, 6]. An alternative strategy to the single oxide phase is to employ two intimately mixed components in which the oxide-ion and electronic conductivity take place in a dual phase¹ system [7]. The advantage of this over single phase MIECs is that two discrete phases can be employed that are more inert than the single MIEC phase (combined ionic and electronic conductivity in a single phase facilitates reduction of the phase and may lead to a phase change). In theory the result may be a comparatively more stable membrane that is less susceptible to degradation processes such as kinetic demixing of constituent cations when employed in an oxygen chemical potential gradient at high temperature. However, in practise; percolation limits, solid state reaction between the two phases, thermal expansion mismatch and cost (noble metals are often used) are drawbacks.

Here we wish to consider membranes which exhibit mobility for two ions simultaneously (here referred to as dual ion conduction). By varying the nature of the mobile ions the membrane function can be modified, raising the interesting possibility of tuning a membrane for selective gas separation by using dual ion conduction in the absence of electronic conductivity. If only one phase is employed then the options for tailoring the membrane are limited, however, dual phase membranes with different ions mobile in each phase can be employed. We will present examples selected from the literature to discuss the underlying transport mechanisms required to realise high temperature dual ion conductivity in single and dual phase membranes.

2. Mechanistic overview.

Transport in single single phase membranes

Recently, perovskite materials showing both oxygen-ion and proton mobility in the absence of electronic conductivity have been shown to be highly selective for water permeation as reported by Coors [8] and Suksamai [9]. The process is initiated by absorption of water via a surface $V_o^{\bullet\bullet}$ to form two hydroxyl groups:

Figure 2 provides a simple pictorial representation of the mechanism for water transport in e.g., the barium cerate oxide system, where $OH_o^\bullet$ represents a proton at an oxygen site in the oxygen sublattice and $V_o^{\bullet\bullet}$ the counter flow of oxygen vacancies. At the permeate side a $V_o^{\bullet\bullet}$ and O_o^x are created as the water is released from the oxide.

¹ The terms “dual phase” and “composite” have both been used in the literature to describe systems in which inorganic components are combined. Here we define this class of membrane as having components that retain their own chemical properties but act in concert to facilitate ion transport.

Figure 2

An important step in describing this mechanism of water permeation was made by Kreuer et al. through development of a model [10, 11] where the chemical diffusion coefficient of water, D_{H_2O} , is determined as a function of temperature and degree of hydration. Neglecting the volume change when water is absorbed, the chemical diffusion coefficient for water (eqn 4) can be related to the chemical diffusion coefficients of oxygen vacancies ($D_{V_O^{\bullet\bullet}}$) and protonic defects ($D_{OH_O^{\bullet}}$) and also the degree of hydration, X , defined as the site fraction of oxygen ion vacancies filled by water molecules.

$$D_{H_2O} = \frac{(2-X)D_{OH_O^{\bullet}}D_{V_O^{\bullet\bullet}}}{XD_{OH_O^{\bullet}} + 2(1-X)D_{V_O^{\bullet\bullet}}} \quad (4)$$

Note that $D_{OH_O^{\bullet}}$ is used rather than $D_{H_i^{\bullet}}$ as the protons reside on oxygen lattice sites. The transference numbers (the fractional contribution to the total conductivity) of oxygen-ion vacancies and protonic defects as a function of water content can be calculated:

$$t_{OH_O^{\bullet}} = XD_{OH_O^{\bullet}} / (XD_{OH_O^{\bullet}} + 2(1-X)D_{V_O^{\bullet\bullet}}) \quad (5)$$

$$t_{V_O^{\bullet\bullet}} = 2(1-X)D_{V_O^{\bullet\bullet}} / (XD_{OH_O^{\bullet}} + 2(1-X)D_{V_O^{\bullet\bullet}}) \quad (6)$$

The model, which does not account for surface kinetics or morphological changes, e.g. surface area loss, was tested by calculating D_{H_2O} from eqn 4 over the temperature range 300 to 900°C and comparing to experimental TGA water incorporation data for (BaO)0.9(CeO₂)0.05(Gd₂O₃). The model was in good agreement with experimental data but indicated slower uptake at higher temperature, possibly due to resistance from the previously reported barium oxide rich grain boundary in these oxides [12], slow surface kinetics or a mass transfer resistance.

If a material exhibits protonic and oxygen-ion transport as well as electron-hole transport then both water and oxygen (as well as hydrogen) can permeate across a membrane formed by the material. Common charge carriers then have a role in both oxygen permeation and water permeation. The concept of coupled “uphill transport” of water in the BaZr_{0.8}Y_{0.2}O_{3-δ} perovskite-type oxide has been proposed based upon non-equilibrium thermodynamic considerations and has been experimentally demonstrated. When the oxygen chemical potential difference across the membrane is sufficiently great oxygen permeation can drive water permeation against its own chemical potential difference [13^{*}, 14].

The single phase need not be solid; a supported single molten phase has been described in a patent from Air Products [15]. Here, nitrite/nitrate ions in the molten phase over the temperature range 429 to 525°C have been used to transport oxygen. The oxygen is incorporated at the feed side forming a nitrate from the nitrite (eqn 7); the nitrate diffuses to the permeate side. The oxygen is released and the nitrite now diffuses to the feed side (eqn 8) ready to form the nitrate species once more (eqn 7).

Transport in dual phase membranes

Dense, oxygen-ion conductors can provide an interconnected three-dimensional pore system in which a guest molten carbonate salt can be infiltrated, resulting in a dual phase membrane that is capable of permeating species.

The concept has been proposed and models to describe the transport of carbon dioxide developed by Wade et al. [16] and Rui et al. [17]. Wade's model can be used to describe the carbon dioxide flux in the absence of surface limitations,

$$J_{CO_2} = \frac{1}{LZ_C} \frac{\frac{\sigma_C}{Z_C}(1-\varepsilon)\frac{\sigma_V}{Z_V}}{\frac{\sigma_C}{Z_C} - (1-\varepsilon)\frac{\sigma_V}{Z_V}} \frac{RT}{F^2} \ln \frac{P_{CO_2}(L)}{P_{CO_2}(0)} \quad (9)$$

as a function of; L , the membrane thickness, $(1 - \varepsilon)$ the volume fraction of the host membrane and ε the volume fraction of molten carbonate. Z_C represents the charge on carbonate ions, Z_V the charge on oxygen vacancies, σ_C represents the conductivity of the carbonate ions and σ_V that of oxygen vacancies. Note that the charge on a vacancy and a carbonate-ion have different signs hence the presence of the minus sign in the denominator of the conductivity/volume fraction term responsible for representing the serial resistances.

The concept has been demonstrated using porous $(ZrO_2)(Y_2O_3)$ (YSZ) and Ce-GdO₂ (CGO) oxygen-ion conductors [18^{••}] hosting eutectic mixtures of $Li_2/Na_2/K_2CO_3$. A schematic of the operation of such a dual phase membrane is shown in Figure 3(a). Gas phase carbon dioxide reacts with lattice oxygen from the oxide creating carbonate-ions that diffuse through the molten salt and oxygen-ion vacancies that diffuse through the solid oxide phase. At the low p_{CO_2} side, carbonate-ions react with oxygen vacancies, releasing carbon dioxide and donating oxygen-ions back to the host oxide.

Figure 3 (a) and (b)

The MIEC $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$ has also been used as a porous host oxide for such a membrane [19^{••}]. However using MIECs as the host permits additional pathways for permeation (Figure 3(b)). In the presence of gas phase oxygen, the MIEC phase can transport oxygen via $V_O^{\bullet\bullet}$ point defects and electronic charge carriers which are not involved in carbonate transport (see also Figure 1). In the presence of gas phase oxygen carbon dioxide transport can also occur. At high temperatures carbon dioxide reacts with gas phase oxygen and electrons (from the MIEC) to form carbonate-ions that become incorporated into the molten phase; at the permeate side the carbon dioxide and oxygen are released, giving up the two electrons back to the MIEC. Through this mechanism we move from dual ionic to ionic (the carbonate) and electronic (the MIEC) charge carriers. We will not discuss this subject further.

Dual phase membranes are challenging to fabricate with problems including inadequate distribution of any sacrificial pore former through the host oxide, loss of molten phase with time [20], reaction between the molten phase and host matrix (demonstrated by work in the 1980s on K_2CO_3 -BaCO₃ which showed that a solid solution can form, e.g., $K_2Ba_4(CO_3)_5$, with implications for host membranes containing barium or strontium [21-23]) and oxidation of the molten salt with time (M_2O formation).

Selectivity remains, to our knowledge, unexplored at the time of this review but we highlight the use of molten carbonates for sulfur dioxide scrubbing in power plants [24]:

The SO_x species can displace the carbonate ion, releasing carbon dioxide into the gas phase. One might expect problems with the selectivity of any carbonate-containing membrane (although depending upon the application this may be beneficial to the process of course) as the sulfur content of the molten phase increases.

Finally, as an aside to the dual ion conduction we have presented, we note that ternary ion conduction has recently been suggested to occur in a molten carbonate fuel cell where carbonate, oxide-ion and protons are

simultaneously transported [25, 26]. It is proposed that protons are transported along the dual phase interface as HCO_3^- species but may also diffuse into the bulk of the carbonate.

Surface exchange at the gas-membrane interface

Transport within the membrane is only one consideration; surface processes are also vital. In the case of an oxide-molten carbonate dual phase membrane the incorporation of carbon dioxide via carbonate formation most likely occurs in the region of the oxide-carbonate interface. An in situ isotopic labelling approach could be a useful tool in determining the role of oxygen associated with the gas phase carbon dioxide, molten carbonate and oxide host. The characteristic length, L_c , indicates the membrane thickness below which the overall transport rate is determined by surface processes and above which by diffusion within the membrane. Once a membrane has a thickness below this characteristic length performance can be improved by increasing the surface area per unit volume in the membrane module. Advances in membrane fabrication methods have produced, e.g., microtubular membranes with high volumetric surface areas [27]. Asymmetric microtubular structures [28] possessing a higher surface area on the side of the membrane that exhibits the rate-determining surface process can also give further improvement.

3. Membrane performance.

The measure of performance of any membrane is the flux that it can provide under realistic operating conditions. Water fluxes through the single phase perovskite $\text{BaCe}_{(1-y)}\text{Y}_y\text{O}_{3-\alpha}$ ($y=0.1, 0.25$) have been carefully measured directly, rather than indirectly by electrical conductivity techniques [9]. This material was able to permeate water with a permeability of $3 \times 10^{-10} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ at 800°C . The model and data of Coors [29] was used to predict the membrane permeation under these conditions (Coors used different hydration equilibria from Kreuer [11] but otherwise the Coors model is similar to the earlier model of Kreuer). The Coors model predicted a permeability of $9 \times 10^{-11} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ at 800°C . The trend in terms of permeation versus temperature shows good agreement between the experimental data and modelling prediction; the higher experimental water permeation rates could possibly due to errors in estimation of leak rates.

For the dual phase carbon dioxide transport membranes, permeabilities of $\text{ca } 6 \times 10^{-12} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ at 800°C have been reported with YSZ and CGO oxide phases, with YSZ having a higher permeability than CGO [18] while the MIEC $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ host provided a permeability of $1\text{--}3 \times 10^{-11} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ at 800°C [19]. In the paper by Wade et al. [18] a comparison was made between the carbon dioxide flux of the YSZ and CGO oxide phases with predicted fluxes derived from their model [16] which assumes solid state conductivities are rate determining. Predicted fluxes were higher than those found experimentally. The lower experimental permeabilities may originate in; slow surface kinetics, low composite conductivities and/or poor estimation of the porosity of the host oxide. The overall structure of the pore network will impact on the transport properties as will the structure of individual pore channels and the solid phase where necking, i.e., reduced cross-sectional area along the channels, may occur increasing resistance at those points. The impact of porosity on conductivity has been modelled and compared to experimental conductivity data for a perovskite ($\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$) and a fluorite ($(\text{ZrO}_2)_{0.9}(\text{Y}_2\text{O}_3)_{0.1}$) with reasonable agreement [30].

Long term stability is an often neglected issue in high temperature membrane technology studies. The dual ion conducting membrane studies we have presented here do not tackle this due to the novelty of the work and their initial proof-of-concept nature. Water permeation has been monitored over several days [9] and carbon dioxide permeability data has been presented over 66 hours [19]. Much longer term studies are required to indicate suitability in applications where membranes will need to operate continuously over longer periods of time.

4. Summary and future directions

It is possible to use a single phase perovskite membrane to transport water. Porous oxides can also be used to host a second phase, creating a dual phase system capable of transporting carbon dioxide in the case of molten carbonate infiltration. The question of whether other species such as SO_x may form sulfite or sulfate ions in such a molten carbonate leading to SO_x transport across the membrane is yet to be answered. If high carbon dioxide selectivities are desired SO_x transport needs to be avoided; if acid gas removal is desired SO_x transport could be beneficial.

Water and carbon dioxide permeable membranes have potential uses in; sensor technology, separation and combined reaction and separation processes. The oxide-carbonate dual phase concept has been suggested as a route to carbon dioxide capture for pre-combustion processes, e.g., following coal gasification [31]. Other potential applications include the removal of carbon dioxide from the water-gas shift reaction to overcome equilibrium and facilitate higher conversions to hydrogen. Delivery of a reactant is also possible; $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ has been used to deliver water into the anode compartment of a fuel cell for steam reforming of methane [8, 32].

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Table Captions

Table 1 Examples of Kröger-Vink notation used to describe lattice point defect species

Tables

example	describes;
$V_O^{\bullet\bullet}$	vacancy at an oxygen site, +2 charge
O_O^x	oxygen at an oxygen site, no net charge
$O_i^{\prime\prime}$	interstitial oxygen, -2 charge
e'	electron, -1 charge (site not specified)
$h^\bullet$	electron hole, +1 charge
$OH_O^\bullet$	proton at an oxygen site, +1 charge
$La_{Sr}^\bullet$	lanthanum at a strontium site, +1 charge

General form is M_S^C where M corresponds to the species (atom, vacancy, electron, hole) ; S the occupied site, "i" represents an interstitial ; C the net charge at the site where "x" represents no net charge, each ' symbol represents -1 and each $^\bullet$ symbol represents +1.

Figure Captions

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Figure 1 Schematic showing a single phase MIEC membrane transporting oxygen-ion vacancies and electrons due to an oxygen chemical potential difference. The reaction at both membrane surfaces is shown in Kröger-Vink notation.

Figure 2 Schematic showing a single phase solid oxide membrane transporting water. The transport mechanism involves protons in motion as interstitial defects, $H_i^\bullet$, hopping between hydroxyl groups (eqn 2) and a counter-current of $V_O^{\bullet\bullet}$ defects transporting oxygen; electronic charge carriers plays no role. The overall reaction at both membrane surfaces is also shown in Kröger-Vink notation.

Figure 3 (a) Schematic showing a dual phase solid oxide-molten carbonate membrane transporting carbon dioxide and (b) parallel pathways available when using an MIEC instead of a pure oxygen-ion conducting host porous oxide. It is possible to transport oxygen alone (i) or in combination with carbon dioxide (ii). The reactions at both membrane surfaces are also shown in Kröger-Vink notation.

Figure 1

Figure 2

Figure 3 (a) and (b)