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Please cite this article as: W. Xing, Z. Li, T. Peters, M-L. Fontaine, M. McCann, A. Evans, T. Norby, R. Bredesen, Improved CO_2 flux by dissolution of oxide ions into the molten carbonate phase of dual-phase CO_2 separation membranes, *Separation and Purification Technology* (2018), doi: https://doi.org/10.1016/j.seppur.2018.11.090

Improved CO₂ flux by dissolution of oxide ions into the molten carbonate phase of dual-phase CO₂ separation membranes

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Abstract

In a solid-liquid dual-phase CO_2 separation membrane, the native ions in the molten alkali carbonate, including carbonate anions and metal cations can transport CO_2 in a process that is charge-compensated by electronic species (electrons or holes), oxide ions, or hydroxide ions, depending on materials and conditions. This strongly affects the design of experiments for assessing the performance of these membranes, and further determines the routes for integration of these membranes in industrial applications. Here we report how dissolved oxides in the liquid carbonate improve the CO_2 flux of the membrane due to an enhanced charge-compensating oxygen ion transport. A qualitative understanding of the magnitude and role of oxide ion conductivity in the molten phase and in the solid support as a function of the temperature is provided. Employing a solid matrix of ceria, and dissolving $CsVO_3$ and MoO_3 oxides in the molten carbonate phase led to an almost doubled CO_2 flux at 550 °C under dry ambient conditions. When the sweep gas contained 2.5% H_2O, the CO_2 flux was increased further due to formation of hydroxide ions in the molten carbonate acting as charge compensating species. Also, as a consequence of permeation controlled by ions in the liquid phase, the CO_2 flux increased with the pore volume of the solid matrix.

Keywords: Dual-phase membranes; CO₂ separation; molten carbonates, solubility of oxides

1 Introduction

Dual-phase CO_2 separation membranes, consisting of a molten alkali metal carbonate phase embedded in a solid matrix that is either an electronically conducting metal or ceramic, or an oxide ion conducting ceramic (mixed conductor or electrolyte type), can provide ambipolar transport for permeation of CO_2 or CO_2 and O_2. The membranes typically operate at temperatures above 500 °C, which is necessary to melt the carbonate phase comprising of eutectic binary or ternary mixture of Li^+, K^+, Na^+ carbonate salts. The flexible transport properties of these membranes have raised interest for application in a number of processes where separation of CO_2 or both CO_2 and O_2 is required. These encompass carbon capture and sequestration (CCS) applications for high temperature CO_2 separation in pre- and post-combustion CO_2 capture processes [1] and oxyfuel combustion, as well as in steam/dry reforming membrane reactors [2, 3]. Various materials for dual-phase membranes have been investigated over the past few years, where focus was given to improving the flux by tailoring the microstructure [4] and transport properties of the solid phase. The latter has been screened among metals such as stainless steel [2], oxide ion conductors (Gd- and Sm-doped CeO_2 [5, 6], Y-stabilized zirconia [5] and $Bi_{1.5}Y_{0.3}Sm_{0.2}O_3$ [7, 8]), mixed electron and oxide ion conductors ($La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ [9]) and non-conductive ceramics such as alumina [5]. A CO_2 flux higher than 1 mL /cm^2 min at 600 °C has been reported for a 1 mm thick dual-phase membrane with Ag as the solid matrix [10]. In this case, with feed gas containing O_2, the transport of carbonate ions charge compensated by electrons in the metal, results in a flux of both CO_2 and O_2.

Much less attention has been directed to improving the properties of the molten carbonate phase, which would be valuable for reducing the operating temperature and/or for further increasing the CO_2 flux while maintaining high CO_2 selectivity. We have recently shown that dissolution of steam into the molten carbonate phase increases the CO_2 flux of a dual-phase membrane with an oxide ion conducting solid matrix of CeO_2 [11]. An approximate 30% increase in the CO_2 flux was obtained when 2.5% steam was introduced to the feed side gas stream, while an increase in the CO_2 flux by a factor of 2.5 to 3 was observed when introducing the same amount of steam to the sweep side. These flux variations were explained by transport of CO_2 via various combinations of charged species including carbonate ions, oxide ions and hydroxide ions which will be discussed in the next section.

In the present work, we focus on the transport properties of molten salt and provide a novel pathway for tailoring the transport properties of the dual-phase membrane via the addition of foreign oxide ions by dissolving MoO_3, $CsVO_3$ into the molten carbonate phase. The role of oxides dissolution on the transport properties of the dual-phase membrane was investigated by both experimental and theoretical approaches.

2 Transport theory for dual phase membranes

The flux through dual-phase CO_2 separation membranes is governed by transport of carbonate ions in the molten carbonate phase and at least one additional ionic and/or electronic charge carrier in the molten phase and/or in the solid porous matrix under an electrochemical potential gradient according to Wagner-type transport theory. The working principle is

therefore similar to mixed conducting dense ceramic membranes for oxygen or hydrogen separation, where oxide ions and protons, respectively, are charge compensated by transport of electrons. These membranes can be made as single-phase materials or composites of ceramic and/or metallic phases which enhance ambipolar transport. Transport in dual-phase membranes normally involves more than one mobile ionic species (carbonate ion, oxide ion and hydroxide ion) and these can charge compensate each other. Thus, electronic charge transport is not necessary for CO_2 permeation, which is different from the dense mixed ion and electron conducting membranes. However, transport of electrons can be involved when an electronically conducting solid matrix is used, and in this case, the dual-phase membrane would show transport of both O_2 and CO_2 [8, 12]. It must be mentioned that the native metal cations in the molten phase are mobile in addition to the carbonate ions. However, these will contribute to transport in a way indistinguishable from carbonate ion transport due to the flow of the liquid salt [13].

A general equation including the possible charged species for describing the CO_2 flux density from the feed to the sweep side of a dual-phase membrane can be written as

$$ j_{CO_2} = j_{CO_3^{2-}} = \frac{RT}{2F^2L} \int_{sweep}^{feed} \sigma_{CO_3^{2-},M^+} \left[\left(t_{O^{2-}} + t_{OH^-} + t_{e^-} \right) d\ln p_{CO_2} + \frac{1}{2} t_{e^-} d\ln p_{O_2} - t_{OH^-} d\ln p_{H_2O} \right] \quad (1) $$

where $\sigma_{CO_3^{2-},M^+}$ is the conductivity of native ions including alkali metal and carbonate ions, L the membrane thickness, p the partial pressure of gases, t the transport numbers, R the gas constant, F the Faraday constant and T the temperature. For simplicity, transport of native ions in the molten phase will hereafter be referred to as carbonate ion transport and conductivity. In the above equation, more complicated ions such as oxycarbonates are not taken into consideration but their possible contributions will be discussed in Section 4 with experimental results.

The type of porous matrices employed in a dual-phase membrane can be classified into four categories according to their transport properties: a pure oxide ion conductor, a pure electronic conductor, a mixed ionic and electronic conductor, and a non-conducting material. Equation 1 can be simplified for each case.

When only oxide ions and carbonate ions contribute, i.e. a support matrix of oxide ion conducting or non-conducting material is used, Eq. 1 can be simplified into

$$ j_{CO_2} = j_{CO_3^{2-}} = \frac{RT}{2F^2L} \int_{sweep}^{feed} \sigma_{CO_3^{2-}} t_{O^{2-}} d\ln p_{CO_2} = \frac{RT}{2F^2L} \int_{sweep}^{feed} \frac{\sigma_{CO_3^{2-}} \sigma_{O^{2-}}}{\sigma_{CO_3^{2-}} + \sigma_{O^{2-}}} d\ln p_{CO_2} \quad (2) $$

The CO_2 flux would be limited by either the carbonate ion or oxide ion conductivity, whichever is lower. In most cases, the oxide ion conductivity of the solid matrix or the molten carbonate phase is much lower than that of native ions in the melt due to mobility or concentration, respectively. It would thus be the oxide ion conductivity of the solid matrix or the molten carbonate phase that will limit the carbonate (and CO_2) flux. In principle, oxide ion

conduction in the molten carbonate can arise from oxide ions generated through the following (interrelated) equilibria

$$CO_3^{2-} = O^{2-} + CO_2(g) \tag{3}$$
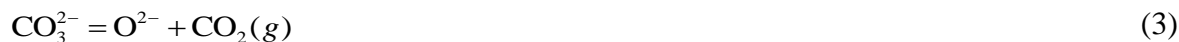
for the molten carbonate itself and through

$$MO_{Z/2} = \tfrac{Z}{2}O^{2-} + M^{z+} \tag{4}$$

for foreign oxides dissolved in the melt, where Z is the charge number of the metal M. In this work, the origin of the oxide ions in the molten carbonate will be signified by denoting them as native and foreign oxide ions, from the molten carbonates and from the dissolved oxides, respectively.

3 Experimental

CeO_2, NiO and Al_2O_3 were used as porous matrices. CeO_2 (Sigma Aldrich, 99.99%) and NiO (Alfa Aesar, 99.995%) powders were used to produce porous matrices by a pressing-annealing method. For varying the porosity of the solid matrix, a powder mixture containing 50 vol.% oxide and 50 vol.% rice starch (food grade) was pressed into pellets with a diameter of 2.1 cm and a thickness of ~1.1 mm. The pellets were annealed at 1350 – 1400 °C for 5 h. The relative density of the porous pellets was calculated from their mass and volume. The alumina matrix was purchased from KeraNor (Norway) and had a pore size of 1 μm and a relative porosity of 33 vol.%.

The molten carbonate phase comprised a eutectic mixture of 62 mol.% Li_2CO_3 (Sigma Aldrich, $\geq$ 99%) and 38 mol.% K_2CO_3 (Sigma Aldrich, 99.995%). To study the contribution of foreign oxide ions, $CsVO_3$ (Alfa Aesar, 99.9%) and MoO_3 (Sigma Aldrich, $\geq$ 99.5%) were firstly pre-mixed at a molar ratio of 3:1 and subsequently added to the eutectic carbonate salt mixture at a weight ratio of 1:5. For infiltration of the carbonate phase, pellets were sealed to the top end of a ~4 mm thick Y-stabilised zirconia tube using Ceramabond™ 671 sealant (Aremco Products Inc., USA). The sealed assembly was slowly heated up in a custom-made dip-coater equipped with a furnace and a larger alumina crucible containing the eutectic carbonate mixture. The carbonate infiltration was performed by slowly dipping the sealed porous sample into the carbonate melt at 600 °C for a few seconds.

Flux measurements were performed in a ProboStat^{TM} cell (NorECs, Norway) and an S-type thermocouple was placed close to the sample inside the measurement cell, which was heated in a vertical tube furnace. Automated mass flow controllers (Bronkhorst High-Tech, the Netherlands) were used to control the gas supply to the feed and permeate sides of the membranes. For the flux measurements, the membranes were firstly heated in a mixture of air and helium up to 400 °C with a heating rate of 120 °C/h. A mixture of CO_2 (99.995%, 10 mL/min), He (99.9995%, 10 mL/min) and N_2 (99.999%, 30 mL/min) was then introduced to the feed side of the membranes (total flow 50 mL/min). In all experiments, helium was present in the feed side as a probing gas for detecting leakages, and N_2 was used as a balance gas. A sweep flow of 30 mL/min of Ar (99.999%) was applied at the permeate side. Both the

feed and permeate side of the membrane were kept at atmospheric pressure for all experiments. Under these conditions, the magnitude of the CO_2 flux has a negligible influence on the feed side gas composition. The CO_2 fluxes were calculated from the concentration of CO_2 in the permeate, monitored by a gas chromatograph (GC, Varian Inc., CP-4900), and the calibrated flow of the Ar sweep gas. The helium content in the sweep was monitored continuously throughout the experiments and remained below the detection limit of the GC. Wet conditions were obtained by bubbling the feed gas mixture through a saturated KBr(aq) solution at room temperature yielding approximately 2.5% H_2O, and dry conditions were obtained by supplying gases directly from gas cylinders, yielding in practical levels of typically 30-50 ppm H_2O [14].

4 Results and discussion

4.1 Evidence of oxide ion transport in molten carbonates by varying porosity of solid matrices

Figure 1 shows the CO_2 permeation at different temperatures with different support porosities together with schematic illustration of the experimental setup. In this case, the used carbonates are without oxides addition. It is clearly shown that the CO_2 flux increases with increasing porosity of the solid matrix. By assuming that the oxide ion conductivity might originate from the lithiated CeO_2 and is limiting for the ambipolar CO_2 transport, an increase in the porosity of the matrix would decrease the oxide ion conductivity that in turn would reduce the CO_2 flux. This is in contradiction to the present experimental results. Therefore, we conclude that either the oxide ion conduction originates from the molten carbonate phase rather than from the solid matrix (the increased volume of porosity contributed to an increased volume of carbonate phase and thereby of oxide ion conduction), or that the carbonate ion conduction is the limiting factor for the ambipolar CO_2 transport under the applied measurement conditions according to Eq. 2.
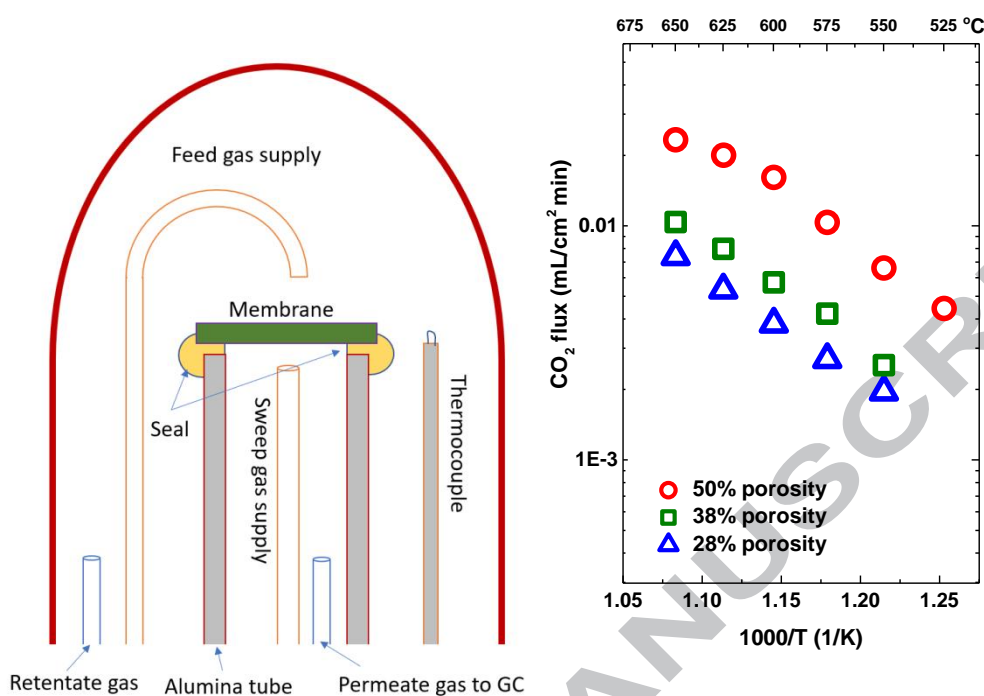
Figure 1: (left) The schematic drawing of the measurement setup. (right) CO_2 flux as a function of inverse absolute temperature with Ceramabond™ as sealants applied to CeO_2 matrices prepared with different porosities. The samples thickness was 1 mm.

4.2 Evidence of oxide ion transport in molten carbonates by varying transport properties of solid matrixes

Figure 2 shows the CO_2 flux measured as a function of the inverse temperature for two membranes prepared by using either a non-conductive porous alumina matrix or a potential oxide ion conductive porous ceria matrix. The carbonates used in this case have no oxides addition. The CO_2 fluxes are fairly comparable despite the slightly higher porosity of the ceria matrix under otherwise identical experimental conditions. Since the alumina support exhibits non-electronic and negligible oxide ion conductivity, this observation provides another strong indication that the oxide ion transport predominately proceeds through the molten carbonate phase rather than the solid phase. For both porous ceria and alumina matrices, the CO_2 transport is barely influenced by the oxygen partial pressure on the feed side at constant partial pressure of CO_2, which follows Eq. 2 for the case of negligible electronic conduction. Similar observations have been reported by Wade et al. [5] at temperatures below 750 °C, whereas oxide ion conduction in the porous solid matrix contributed significantly to the CO_2 flux at higher temperatures.
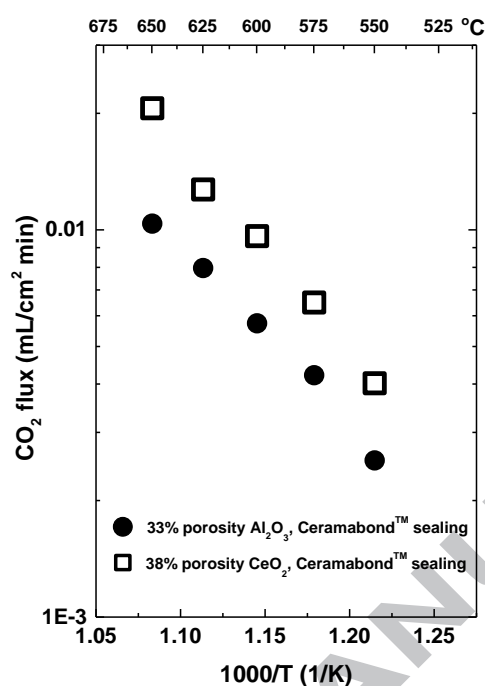
Figure 2: Comparison of CO_2 flux measured for membranes prepared with ceria and alumina matrix sealed with Ceramabond™. Both samples are 1 mm thick. Feed gas is a mixture of CO_2 (99.995%, 10 mL/min), He (99.9995%, 10 mL/min) and N_2 (99.999%, 30 mL/min); sweep gas is 30 mL/min of Ar (99.999%).

Figure 3 shows the fluxes of both CO_2 and O_2 as a function of temperature for a dual-phase membrane with a porous matrix of electron hole conducting NiO with a porosity of 35%. The feed side consisted of a mixture of either 20% CO_2 balanced with He and N_2 or a mixture consisted of 20% CO_2 with 20% O_2 balanced He and N_2. The measured CO_2 flux was higher at all temperatures with both CO_2 and O_2 in the feed, and was accompanied with O_2 permeation. Without oxygen at the feed, only CO_2 was detected on the permeate side.

When there is no O_2 present in the feed, the CO_2 flux results from the ambipolar transport of carbonate ions and oxide ions. Since NiO is not an oxide ion conductor under the measurement conditions, the only path for oxide ion conduction is through the molten carbonate phase. This again confirms that the oxide ion transport through the molten carbonate phase facilitates but is also rate limiting for the CO_2 flux of this membrane under these experimental conditions.

When co-feeding CO_2 and O_2, the obtained CO_2 flux comprises contributions from the ambipolar transport of carbonate ions and oxide ions and the ambipolar transport of carbonate ions and electron holes. In principle, the latter would result in CO_2 and O_2 fluxes at a ratio of 2:1. In Table 1, we have calculated the CO_2 flux resulting from the ambipolar transport of carbonate ions and electron holes by the difference in the CO_2 flux obtained with or without O_2 present in the feed, and we compared this value with the O_2 flux. The ratios between the

calculated CO_2 flux and the measured O_2 flux, 1.7-2.1, are close to the theoretical value of 2 for pure CO_3^{2-} transport. Minor deviations from the value of 2 might be due to insignificant transport from other types of carbonate ions. For instance, if transport of oxycarbonate, CO_4^{2-}, is involved in addition to CO_3^{2-} as reported in Ref. [10], the CO_2 to O_2 ratio would be lower than 2. In the case of dominating CO_4^{2-} transport, the theoretical ratio between CO_2 and O_2 transport would be 0.67 due to the following equilibrium:

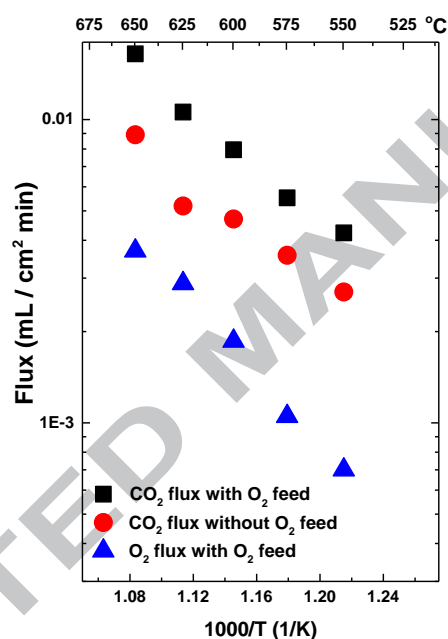$$CO_2(g) + \frac{3}{2}O_2(g) + CO_3^{2-} + 2e^- = 2CO_4^{2-} \tag{5}$$

Figure 3: CO_2 and O_2 flux of a dual-phase membrane with NiO solid matrix measured as a function of the inverse temperature. The feed side gas mixtures were 20% CO_2 + 20% He + 40% N_2 + 20% O_2 (denoted "with O_2 feed") or 20% CO_2 + 20% He + 60% N_2 (denoted "without O_2 feed").

Table 1: The CO_2 flux contributed from different ambipolar transport processes for CO_2 and O_2 at different temperatures with NiO solid porous matrix. The unit for all the flux values is 10^{-3} mL/cm^2 min

	550 °C	575 °C	600 °C	625 °C	650 °C
CO_2 flux I (with oxygen feed)	4.2	5.5	8.0	10.6	16.5
CO_2 flux II (without oxygen feed)	2.7	3.6	4.7	5.2	8.9
CO_2 flux I - CO_2 flux II	1.5	1.9	3.3	5.4	7.6

(CO_2 flux from carbonate ion and electron hole transport)					
O_2 flux	0.7	1.1	1.9	2.9	3.7
(CO_2 flux I - CO_2 flux II) / O_2 flux	2.1	1.7	1.7	1.9	2.1

4.3 Effect of dissolved oxides and hydroxide ions in the molten carbonate

From the experimental results presented above, we conclude that the oxide ion conductivity in the molten carbonate limits the ambipolar conductivity and thus the CO_2 flux of the dual-phase membranes at relatively low operating temperature (below 650 °C). One approach for increasing the CO_2 flux at such low temperatures would therefore be to improve the oxide ion conductivity of the molten carbonate phase. The concentration and conductivity of oxide ions in the molten carbonate phase can be increased by dissolving oxides according to Eq. 4. Previous reports have shown that addition of $CsVO_3$ and MoO_3 to molten carbonate mixtures can improve the electrochemical performance of molten carbonate electrolytes due to the increased oxide ion conductivity [15]. Figure 4 shows CO_2 permeation for a dual-phase membrane prepared with additional $CsVO_3$ and MoO_3 dissolved in the molten phase, and measured under high and low steam conditions at 550 °C.
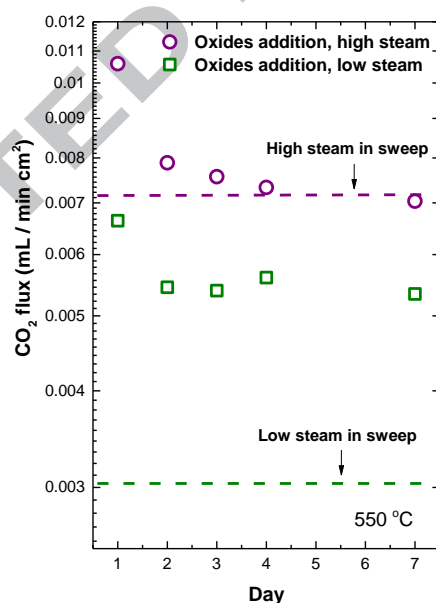

Figure 4: CO_2 flux of CeO_2 supported membranes with $CsVO_3$ and MoO_3 dissolved in the molten phase measured versus time under low and high steam operation conditions. The corresponding CO_2 fluxes without dissolved oxides are marked by dashed lines. The thicknesses of the samples were ~1 mm. Feed gas is a mixture of CO_2 (99.995%, 10 mL/min), He (99.9995%, 10 mL/min) and N_2 (99.999%, 30 mL/min); sweep gas is 30 mL/min of Ar (99.999%).

Under dry conditions (30-50 ppm H_2O), the membrane with addition of oxides shows a significantly higher CO_2 flux as compared to the equilibrium data for the membrane without addition of oxides. This could therefore directly be related to the increase of oxide ion conductivity in the molten phase. The CO_2 flux reached a stable value after approximately one day under operation and was about two times higher than that of the pristine (not containing foreign ions) membrane. On the other hand, with high steam content in the sweep (2.5% H_2O), both the pristine membrane and the membrane with addition of oxides showed similar CO_2 flux at equilibrium. This can be explained by water dissolution according to the following equilibrium:

$$H_2O(g) + CO_3^{2-} = 2OH^- + CO_2(g) \tag{6}$$

whereby the ambipolar transport of carbonate ions and hydroxide ions dominates the CO_2 flux, as previously reported in [12].

The solubility of foreign oxides into the molten carbonate increases with increasing temperature and amounts to tens to hundreds ppm [16]. The contribution from the oxide ions is far from that of the molten carbonate and oxide ion conducting solid matrices. At low temperatures, the intrinsic oxide ion conductivity in the molten carbonate predominates. With increasing temperature, the oxide ion conduction in both the molten carbonate phase (native oxide ions and foreign oxide ions from dissolved oxides), and the solid matrix increases. If the activation energy of the oxide ion conductivity in the solid matrix is higher than that of the carbonate, the membrane performance in terms of CO_2 flux would shift from an intrinsic oxide ion conducting regime to an extrinsic oxide ion conducting regime at higher temperatures. Therefore, the significantly enhanced CO_2 flux by addition of oxides as observed in this work would only be observed at relatively low temperatures.

4.4 Possibility of neutral CO_2 dissolution and transport

Although we believe that the CO_2 flux we obtained in this work is resulting from ambipolar ionic transport, the neutral CO_2 dissolution and transport could also contribute to the overall CO_2 flux. Since solubility of CO_2 in molten carbonates has been determined by different experiment techniques and the values are not in agreement with each other by orders of magnitudes as shown in the reference [17], we have included all the available data in the calculation of neutral CO_2 flux. As we can see in Figure 5, the highest calculated neutral CO_2 flux is about one order of magnitude lower than the experimental obtained flux data in this work, meaning that the neutral CO_2 dissolution and transport is negligible as compared to the ambipolar ionic CO_2 transport.
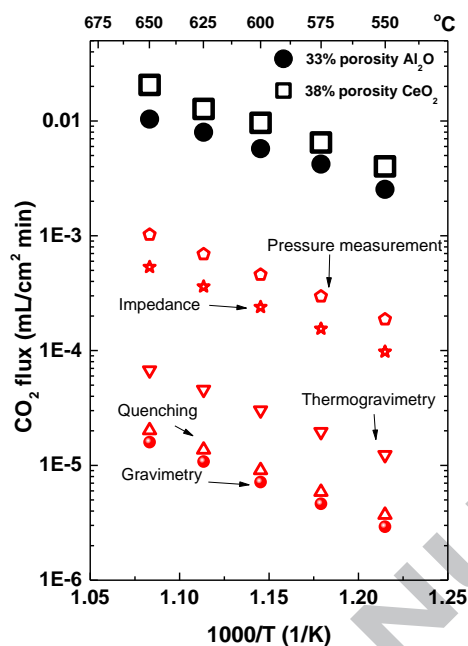
Figure 5: Calculated neutral CO_2 flux based on the reported CO_2 solubility using different measurement methods and diffusion coefficients. The calculated flux is compared with the experimental measured data in this work as shown in Figure 2.

5 Conclusions

The charge compensating oxide ion conduction that facilitates the CO_2 flux in dual-phase membranes consisting of molten carbonate in a solid oxide matrix has been found to take place mostly in the molten carbonate phase at temperatures between 550 and 650 °C. This based on the observation that the CO_2 flux increases with increasing porosity (hence more molten phase) of the matrix, and observed CO_2 flux in non-conductive Al_2O_3 matrix. Accordingly, by dissolving $CsVO_3$ and MoO_3 in the molten phase, the CO_2 flux was increased significantly under dry operating conditions due to increased concentration and conduction of oxide ions in the molten carbonate. The presence of steam increases the CO_2 flux due to dissolution of hydroxide ions resulting in increased ambipolar carbonate ion and hydroxide ion conductivity. Neutral CO_2 transport could contribute to the total CO_2 flux, but the contribution is orders of magnitude lower than from ambipolar ionic transport.

6 Acknowledgement

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Highlights

- Oxide ion conduction in molten carbonates is significantly contributing between 550 to 650 °C.
- Dissolving oxides in molten carbonates can improve CO_2 flux under dry condition.
- Stable operation of the membrane with CuO addition was demonstrated.