Oxygen Ion Transport in Molten Oxide Membranes for Air Separation and Energy Conversion

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Molten oxide membranes (MOMs) are a new class of ion transport inorganic membranes which demonstrate superior oxygen selectivity and permeability and could be used in electrochemical devices such as molten oxide fuel cells (MOFCs) and oxygen separators for energy conversion and air separation, respectively [Acc. Chem. Res., 50, 273 (2017)]. However, oxygen ion transport mechanisms in MOM materials are not clear enough. Understanding the oxygen ion transport mechanisms in molten oxides is important for the discovery of new MOM materials with enhanced performances that can enable the operation of the electrochemical devices more efficiently. Here we suggest an approach that adapts a dynamic polymer chain model, developed for specific molten oxides, to a wide range of melts. This generic model can evaluate the oxygen permeation fluxes through different MOM materials that are comparable to experimental data.

The study of ion transport membrane (ITM) materials and processes is a rapidly expanding research interest field. This is due to the fact that the ITM-based technology modules have the potential to improve the efficiency and environmental performances of energy generation systems. ITM can separate high purity oxygen from air at elevated temperatures and have the potential to reduce the cost of oxygen production in comparison with the conventional cryogenic process. The mixed-conducting perovskite-type compounds, ceramic composites, and cermets are used as ITM materials. The practicalities for incorporating ceramic membrane materials into industrial processes are discussed in comprehensive reviews.

Recently, the molten oxide membrane (MOM) materials have been developed. This MOM materials consist of solid grains and intergranular liquid channels. The intergranular liquid channels provide the membrane material high ionic conductivity, gas tightness, and ductility. This last property allows us to deal successfully with the problem of thermal incompatibility (difference in coefficient of thermal expansion, CTE).

There are two groups of MOM materials, which include molten Bi2O3 or V2O5, in particular, (i) NiO-Bi2O3, In2O3-Bi2O3, CoO-Bi2O3, ZnO-Bi2O3, and Bi2O3-Bi2O3; (ii) ZrO2-V2O5, CuO-V2O5, Bi2O3-V2O5, and TeO2-V2O5. Transport properties (electrical conductivity, oxygen ion transport number, and oxygen and nitrogen permeation fluxes) of these MOM materials have been measured. These membrane materials showed high oxygen selectivity and permeability. The ease of the MOM materials fabrication, combined with competitive oxygen permeability and superior oxygen selectivity, demonstrates a promising application.

Understanding the oxygen ion transport mechanisms in molten oxides is important for the discovery of new MOM materials that can enable the oxygen separation and energy conversion more efficiently. Recently, a dynamic polymer chain model for oxygen ion transport in molten V2O5 has been developed. In this paper, we suggest an approach that adapts the dynamic polymer chain model to a wide range of melts. This generic model can predict the gas permeation fluxes through molten oxide and carbonate membrane materials that are comparable to experimental data.

Oxygen Permeation Flux

The main points of a dynamic polymer chain model are:

(i) a polymer structure is typical for V2O5 melt;
(ii) the polymer chain average length is a function of temperature;
(iii) the disconnection and connection of chains takes place (this process occurs stochastically);
(iv) a chain disconnection leads to the two new chain formation; an oxygen pseudo-vacancy is also formed at the end of one of new chains;
(v) the chains connection leads to the deallocation of one of two terminal ions of oxygen;
(vi) this free oxygen ion takes up a nearest pseudo-vacancy;
(vii) the most mobile charge carriers in the molten oxide material are electrons and oxygen ions;
(viii) the ambipolar conductivity of electrons and oxygen ions (chemical diffusion) limits the oxygen permeability through the molten oxide material;
(ix) the migration of oxygen ions and electrons occurs so that the overall current through the molten oxide material is zero.

According to this model, oxygen permeation flux (jO2) through MOM is generally described by Equation 1:

\[ j_{O_2} = \frac{RT}{4Fz_i^2 \tau_i} \ln \frac{P_{O_2}}{P_{O_2}^\prime} \]  

where \( R \) is the universal gas constant, \( T \) is the temperature, \( \tau_i \) is the oxygen ion transport number of MOM, \( \sigma \) is the ionic conductivity of MOM, \( P_{O_2} \) and \( P_{O_2}^\prime \) are the oxygen partial pressures at the oxygen-rich and -lean sides of the membrane, respectively, \( F \) is the Faraday constant, \( z_i \) is the ion charge number, and \( h \) is the membrane thickness. It is established that the intergranular liquid channels predominantly conduct the oxygen ions in MOMs. Ionic conductivity (\( \sigma_i \)) of the intergranular liquid channels (oxide melt) can be expressed by Eq. 2:

\[ \sigma_i = u_i |z_i| c_i F \]  

where \( u_i \) is the oxygen ion mobility and \( c_i \) is the oxygen ion concentration in melt. According to the Nernst-Einstein equation, the oxygen ion mobility can be written as

\[ u_i = \frac{D_i |z_i| F}{RT} \]

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where $D_i$ is the oxygen ion diffusion coefficient. Substituting Eq. 3 into Eq. 2, the oxygen ionic conductivity can be expressed as follows

$$\sigma_i = \frac{D_i \epsilon_i^2 F^2}{RT}$$

[4]

Since the liquid phase percolates through MOM (Fig. 1), the ionic conductivity of the MOM can be evaluated by Eq. 5

$$\sigma = \eta \sigma_i$$

[5]

where $\eta$ is the volume fraction of liquid. Using Eqs. 1, 4, and 5, we obtain the expression for the oxygen flow in following form

$$j_O = \frac{(1 - \tau_x) c_i \eta D_i}{4 h} \ln \frac{P_{O_2}}{P_{O_2}'}$$

[6]

### Modeling

**Structure.**—According to the literature data, \(^\text{30}\) solid V\(_2\)O\(_5\) consists of the layers of distorted trigonal bipyramids VO\(_5\) whereas vanadium cations are in highly distorted oxygen octahedra. Structure of V\(_2\)O\(_5\) melt and based on it binary oxide systems were studied by X-ray diffraction (XRD), neutron diffraction, nuclear magnetic resonance (NMR), etc.\(^\text{31,32}\) It was established that the intramolecular coordination of atoms changes insignificantly during V\(_2\)O\(_5\) melting. Apparently, the partial rupture of the weakest bond V-O\(_{33}\) occurs thereby forming first two-dimensional layers and followed by chains formation. Thus, chains consisting of distorted tetrahedra VO\(_4\) or trigonal bipyramids VO\(_5\) exist in glass-like oxide melts based on V\(_2\)O\(_5\) (Fig. 2a).\(^\text{34}\) The average number of structure units (N) in chain depends on temperature and is about 120 at 700 °C.\(^\text{35}\)

Oxide glasses based on Bi\(_2\)O\(_3\) in solid and molten state have been studied a lot using atomic absorption spectroscopy (AAS), XRD, infrared spectroscopy (IR), Raman spectroscopy, electron paramagnetic resonance spectroscopy (EPR), X-ray photoelectron spectroscopy (XPS) etc.\(^\text{36–43}\) It has been found that Bi\(_2\)O\(_3\) forms trigonal pyramids BiO\(_3\) (with Bi apex) or distorted octahedra BiO\(_6\) in glasses (Fig. 2b). Milanova et al.\(^\text{43}\) based on IR-spectroscopy results, conclude that bismuth oxide is represented as only BiO\(_n\) polyhedra. Taking into account the fact that structure of any compounds in molten and glass state is similar, it can be assumed that the same structure units (BiO\(_3\) or BiO\(_6\)) will be contained in melts based on bismuth oxide.

**Oxygen transport.**—Let us consider the oxygen transfer in oxide melt under an oxygen electrochemical potential gradient. Scheme of this process is presented in Fig. 3. On the melt surface with low oxygen partial pressure ($P_{O_2}^A$) separation of terminal oxygen anion from chain occurs, followed by the formation of the molecular oxygen (step 1; $O_2 = V_0 + 2e^- + \frac{1}{2}O_2$). This formed pseudo-vacancy of oxygen ($V_0'$) interacts with the bridging oxygen atom of another chain, results in complete chain with bridging oxygen and chain with pseudo-vacancy of oxygen at the end (step 2; $V_0' + O_2 \leftrightarrow O_2 + V_0$). Thus, one can represent the oxygen transfer as consistent connections-disconnections of chains in the melt (repetition of step 2). On the other melt surface with high oxygen partial pressure ($P_{O_2}^C$) pseudo-vacancy of oxygen ($V_0$) interacts with chemisorbed from the gas phase oxygen to form a complete chain (step 3; $V_0 + 2e^- + \frac{1}{2}O_2 = O_2$). Electronic conductivity of oxide melts was considered by Pastukhov et al.\(^\text{36}\)

According to the model, only one oxygen pseudo-vacancy is located at the end of one of two chains, each of which contains N metal atoms (or N structure units) and $\frac{xN}{2}$ oxygen atoms ($x$ is the metal oxidation state). Therefore, the concentration of oxygen pseudo-vacancies (or charge carriers) ($c_i$) is $(2 \times \frac{xN}{2})$ times less than the concentration of oxygen atoms in oxide melt ($c_m$)

$$c_i = \frac{c_m}{xN}$$

[7]

The concentration of oxygen atoms in oxide melt can be determined knowing the density ($\rho$) and the molar mass of oxide ($M$)

$$c_m = \frac{x \rho}{2M}$$

[8]

As a result, in our model, the charge carrier concentration ($c_i$) depends neither on the type of structure units that forms the chain, nor on the oxidation state of the metal.

$$c_i = \frac{\rho}{2MN}$$

[9]

Using Eqs. 6 and 9, the oxygen permeation flux could be expressed as follows

$$j_O = \frac{(1 - \tau_x) \rho \eta D_i}{8MNh} \ln \frac{P_{O_2}}{P_{O_2}'}$$

[10]

Equation 10 can be used to calculate the oxygen permeation fluxes in both polymer ($N >> 1$) and non-polymer ($N = 1$) melts. The calculated and experimental values of oxygen permeation fluxes are

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**Figure 1.** BSEM image of the fracture face of Co\(_3\)O\(_4\)-36 wt% Bi\(_2\)O\(_3\) MOM material after cooling from 850 °C confirming the percolation of liquid phase (light constituent).

**Figure 2.** Structure units of oxide melts based on (a) V\(_2\)O\(_5\) and (b) Bi\(_2\)O\(_3\).

**Figure 3.** Scheme of oxygen ion transport in oxide melt.
presented in Table I. The mean absolute percentage deviation (MAPD) of our calculation is equal 19%. In addition, the carbon dioxide permeation flux through LCCF-(Li/Na/K)xCO3 molten carbonate membrane was also evaluated

\[ j_{C_{2}O_{2}} = \frac{\rho_{2}D_{2}}{8MNc} \ln \left( \frac{P_{C_{2}O_{2}}}{P_{O_{2}}} \right) \]  \[ [11] \]

where \( \rho \approx 2000 \text{ kg/m}^3 \), \( \eta \approx 0.5, D_{2} = 6.50 \times 10^{-8} \text{ cm}^2/\text{s} \), \( M \approx 0.1 \text{ kg/mol}, N = 1, h = 1.25 \text{ mm} \), \( \ln \left( \frac{P_{C_{2}O_{2}}}{P_{O_{2}}} \right) \approx 0.24 \), and the electron transport number \( \tau_e \approx 1 \). The estimated value is \( 3.8 \times 10^{-8} \text{ mol/(cm}^2 \text{s}) \) which is the same order of magnitude with experimental one \( 5.5 \times 10^{-8} \text{ mol/(cm}^2 \text{s}) \). Thus, the calculated values of oxygen and carbon dioxide permeation fluxes through MOM and MCM materials, respectively, are in agreement with experiment.

**Conclusions**

We have adapted a dynamic polymer chain model to a wide range of oxide melts. The calculated, in the framework of this generic model, oxygen permeation fluxes through different MOM materials are in agreement with experimental data indicating the adequacy of the model. The generic model can predict oxygen permeation fluxes through both polymer and non-polymer melts and, therefore, can be successfully used for the search and development of new MOM materials that can enable the operation of electrochemical devices such as molten oxide fuel cells (MOFCs) and oxygen separators more efficiently.

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