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A Computer Simulation of the Oxygen Reduction Reaction in Carbonate Melts

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ABSTRACT

A computer simulation of the oxygen reduction reaction in various carbonate melts has been carried out under steady-state conditions on the basis of a proposed kinetic model which takes into consideration the autocatalytic reaction involving oxygen and other reducible oxygen species in the melt, and the neutralization of oxide ions by dissolved carbon dioxide. A simulation of the presence of (physically) dissolved oxygen, in the diffusion layer region of the melt, corresponding to the possible situation in porous electrodes, causes a significant enhancement in the polarization curves, particularly in the kinetic limiting (CO2 neutralization) region. High rates of the autocatalytic and neutralization reactions display the same effects on the polarization curves as dissolved O2 and CO2, respectively, but to a lesser degree. Comparison of the simulated polarization curves in various carbonate melts indicates that Li-rich melts show the best kinetic performance. On the contrary, the highest limiting currents are observed in K- or Na-rich melts. Variation of the cation composition in Li/K carbonate melts indicates that melts of high Li-content should give better kinetic performance.

The development of the molten carbonate full cell (MCFC) has been hindered partly by problems associated with the oxygen cathode. The severe material problems associated with the oxygen reaction, particularly at the high operating temperatures (>600°C) of the MCFC, the complexity of the O2 reduction reaction and the polarization losses caused by the slow kinetics of this reaction are some of the crucial problems that have to be resolved in order to develop an effective and efficient oxygen cathode as an integral part of the MCFC. The basis for resolving these problems lies in the elucidation of the kinetics of the cathode reaction.

Efforts to elucidate the kinetics of the oxygen cathode in the MCFC have been in progress since the early 1970s. However, to date, the actual nature of the reaction mechanism has not been fully resolved. Appleby and Nicholson gave evidence that (1-4) oxygen dissolves in alkali carbonate melts primarily as a mixture of peroxide (O2-) and superoxide (O2-) ions; the relative amounts of these ions depend strongly on the composition of the alkali carbonate melt. The presence of superoxide ions has been confirmed in pure Li2CO3 or Li-rich melts (2); whereas

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Peroxide mechanism

\[ \frac{1}{2} \text{O}_2 + \text{CO}_2 = \text{O}_2 + \text{CO}_2 \]
\[ \text{O}_2 + e^- = \text{O}_2^- + \text{O}^- \]
\[ 2 \text{O}_2^- + 2\text{CO}_2 = 2\text{CO}_2^- \]

Superoxide mechanism

\[ \frac{3}{4} \text{O}_2 + \frac{1}{2} \text{CO}_2 = \text{O}_2 + \frac{1}{2} \text{CO}_2 \]
\[ \text{O}_2 + e^- = \text{O}_2^- \]
\[ \frac{2}{3} \text{O}_2^- + 2e^- = 2\text{O}_2^- \]
\[ 2 \text{O}_2^- + 2\text{CO}_2^- = 2\text{CO}_2^- \]

In addition, a third mechanism, “the percarbonate mechanism,” based on the hypothetical percarbonate ion, has occasionally been considered in the literature (8, 9). However, none of these mechanisms has been found to be unambiguously consistent with experimental results, especially those from porous electrodes.

Conflicting conclusions persist in the literature about the dominant species in alkali carbonate melts, the true nature of the reaction mechanisms, and the values of the kinetic parameters. For example, Appleby and Nicholson (4) considered that peroxide and superoxide ions are reduced successively by a 3e- and a 1e- step in Li/K and Na/K carbonate melts whereas Vogel et al. (6) concluded that the reduction appears to be complete in a single superoxide wave by a 3e- process in Li/K melt. The exchange current densities evaluated by Lu (16), Yuh (8), and Uchida et al. (11) for the O2 reduction reaction at a gold electrode in Li/K melt by the potential-step method were two orders of magnitude greater than the values obtained by Appleby and Nicholson (4) using potential sweep. The reported reaction orders for O2 and CO2 also vary (5, 12-14). Yuh (8) found the oxygen cathode to be under mixed reaction control, while other investigators have analyzed their results either in terms of a fully reversible process (3, 11, 15) or as one with completely irreversible kinetics (6, 7, 16). The reason for the conflicting results can partly be attributed to the basic assumptions made in analysis of the results. For example, even if the peroxide or superoxide ion is the dominant species in the melt, both species should be taken into consideration in the analysis of the results, since they may be involved successively. Similarly, completely reversible or irreversible kinetics should not be applied in the analysis of the results when mixed kinetics may best describe the data.

The complexity of the sequence of reactions at the O2 cathode makes the traditional approach of deciphering the kinetics of this reaction system solely via experimentation very cumbersome. Computer simulation provides a rapid and direct way of gaining insight into the behavior of such a complex reaction system. Digital simulation can complement experimentation by (i) defining a priori the parameters necessary for the efficient design of experiments, and by (ii) serving as an important diagnostic tool in the analysis and interpretation of experimental data.

In this paper, the reaction sequences for oxygen reduction in MCFCs are simulated under conditions similar to those employed experimentally using bulk melts. The simulations were carried out at a rotating disk electrode (RDE), primarily because of its well-defined hydrodynamics and ease of modeling (17). The conditions in a porous electrode are simulated by allowing the effective molecular dioxygen concentration to vary outside the diffusion layer to simulate a gas atmosphere. Therefore, the objectives of this work are to predict (i) the effect of the autocalytic and the neutralization reactions on the polarization curves, (ii) the effect of different cations and their compositions in the melt on the polarization data, and (iii) the effects of dissolved gases (molecular oxygen and carbon dioxide) on the steady-state polarization currents.

Model Development

Kinetic model—The kinetic model combines the 2e- reduction of O2 with the 1e- reduction of O2 ions proposed by Appleby and Nicholson (3, 4). The first step in this model involves the chemical dissolution of oxygen in the melt to form peroxide (O2) and superoxide (O2-) ions, as in equilibrium reactions [1] and [2] at the gas-melt interface

\[ \frac{1}{12} \text{[O}_2 + 2\text{CO}_2^- = 2 \text{O}_2^- + 2\text{CO}_2] \]
\[ \frac{1}{6} \text{[O}_2 + \text{O}_2^- = 2 \text{O}_2^-] \]
\[ 2 \text{[O}_2^- + \text{O}_2^- = 2 \text{O}_2^-] \]
\[ 1/6 \text{[3/2 O}_2 + \text{O}_2^- = 2 \text{O}_2^-] \]
\[ 7/6 \text{[O}^- + \text{CO}_2 = \text{CO}_3] \]
\[ 1/2 \text{O}_2 + \text{CO}_2^- + 2e^- = \text{CO}_3^- \]

It must be noted that the sum of reactions [1] and [2] leads to the usual representation of the superoxide formation reaction in Eq. [2A]

\[ 1/12 \text{[3 O}_2 + 2\text{CO}_2^- = 4 \text{O}_2^- + 2\text{CO}_2] \]

The O2 and O2- species formed at the electrolyte-gas interface then diffuse to the electrode surface where they are reduced by the electrochemical reactions in Eq. [3] and [4]. The oxide ions (O-) formed in reaction [3] can be neutralized by dissolved CO2 in the melt according to reaction [6]. However, this neutralization reaction has been found to be slow and may possibly be rate limiting (10). Therefore, a buildup of O- ions in the vicinity of the electrode may occur leading to changes in the acid-base properties of the melt and, consequently, to changes in the local electrode potential (2-4). A presence of dissolved oxygen (O2) in the melt can lead to an autocatalytic reaction involving dissolved oxygen and a reducible oxygen species such as O2- in the melt as represented by Eq. [5]. There is as yet no evidence to support the presence of dissolved oxygen in bulk melts (1, 5). However, the situation may be quite different in porous electrodes where the dissolution zone for molecular oxygen in the melt could extend into the thin electrolyte film/meniscus in contact with the catalyst layer. For the bulk melt case, it is assumed that all of the oxygen that dissolves in the melt reacts immediately with the melt according to Eq. [1] and [2] at the melt-gas interface, so that no dissolved oxygen would exist in the reaction zone. Both this case, as well as the more general case where some unreacted dissolved oxygen exists in the bulk electrolyte which perhaps occurs in porous electrodes, are considered here. The sum of the sequence of reactions in Eq. [1]-[6] yields the half-cell reaction in Eq. [7] for the overall reduction of oxygen in the molten carbonate fuel cell.

The model equations for the kinetic rate processes are given below. Reactions [1] and [2] are assumed to be very rapid and therefore, they can be represented by the equilibrium expressions in Eq. [8] and [9], respectively

\[ K_1 = \frac{c^2_{\text{CO}_2} c^3_{\text{CO}_3}}{p_{\text{CO}_2}^2 p_{\text{CO}_3}} \]
\[ K_2 = \frac{c^2_{\text{O}_2^-} p_{\text{CO}_2^-}}{p_{\text{O}_2} p_{\text{CO}_2}^-} \]

The homogeneous reactions occurring in melt are represented by the following rate equations

\[ r_\phi = -k_{\text{ef}} c_{\text{CO}_2} - k_{\text{O}_2^-} c_{\text{CO}_2^-} + k_{\text{O}_2^-} p_{\text{O}_2^-} \]
\[ r_N = -k_{\text{ef}} c_{\text{CO}_3} + k_{\text{CO}_2^-} p_{\text{CO}_2^-} \]
where the net rate of consumption/production of a species $i$ involved in the homogeneous reactions is denoted by

$$R_i = \sum_j s_{ij} f_j$$  \[11\]

The derivation of the kinetic rate expressions for the electrochemical reactions in Eq. [3] and [4] is given in the Appendix. The rate equations for these two reactions are given by Eq. [A-22] and [A-24],

$$i_3 = i_{3,\text{ref}} \left[ \frac{C_{O_2}}{C_{O_2,\text{ref}}} \right]^a \exp \left( \frac{\alpha_3 F}{RT} \eta \right) - \frac{C_{O_2}}{C_{O_2,\text{ref}}} \exp \left( \frac{-\alpha_3 F}{RT} \eta \right)$$  \[A-22\]

$$i_4 = i_{4,\text{ref}} \left[ \frac{C_{O_2}}{C_{O_2,\text{ref}}} \right]^b \exp \left( \frac{\alpha_4 F}{RT} \eta \right) - \frac{C_{O_2}}{C_{O_2,\text{ref}}} \exp \left( \frac{-\alpha_4 F}{RT} \eta \right)$$  \[A-24\]

The overall current density is the sum of the partial current densities in Eq. [A-22] and [A-24], that is

$$i = i_3 + i_4$$  \[12\]

The above rate expressions are assumed to occur in K-rich or Na-rich carbonate melts such as Li/K, Li/Na/K, Li/Na, and Na/K, in which both O$_2$ and O$_{\text{red}}$ species are known to exist (7). On the contrary, only O$_2$ species have been established to be present in Li$_2$CO$_3$ melts (2). Therefore, the following reaction sequence was proposed for Li$_2$CO$_3$

$$1/3 \text{Li}_2\text{O} + 1/3 \text{CO}_2 \rightarrow \text{CO}_2$$  \[1\]

$$1/3 \text{Li}_2\text{O} + 1/3 \text{CO}_2 \rightarrow 2/3 \text{Li}_2\text{O}_2$$  \[2\]

$$1/3 \text{Li}_2\text{O} + 1/3 \text{CO}_2 \rightarrow 2/3 \text{Li}_2\text{O}_2 + 1/3 \text{O}_2$$  \[3\]

$$1/3 \text{Li}_2\text{O} + 1/3 \text{CO}_2 \rightarrow 2/3 \text{Li}_2\text{O}_2 + 1/3 \text{O}_2$$  \[4\]

$$1/3 \text{Li}_2\text{O} + 1/3 \text{CO}_2 \rightarrow 2/3 \text{Li}_2\text{O}_2 + 1/3 \text{O}_2$$  \[5\]

$$1/3 \text{Li}_2\text{O} + 1/3 \text{CO}_2 \rightarrow 2/3 \text{Li}_2\text{O}_2 + 1/3 \text{O}_2$$  \[6\]

$$1/3 \text{Li}_2\text{O} + 1/3 \text{CO}_2 \rightarrow 2/3 \text{Li}_2\text{O}_2 + 1/3 \text{O}_2$$  \[7\]

Material balance equations at the RDE.—A mass balance on species $i$ within the diffusion layer of a RDE yields (18)

$$\frac{\partial c_i}{\partial t} = - \nabla \cdot \mathbf{N}_i + R_i$$  \[13\]

where the flux of species $i$ is given by the sum of the migration, the diffusion, and the convection terms

$$\mathbf{N}_i = - z_i F c_i \nabla \phi - D_i \nabla c_i + c_i \mathbf{v}$$  \[14\]

Substitution of the $y$-component of $\mathbf{N}_i$ in Eq. [14] into Eq. [13] with further simplification (17, 18) leads to the final one-dimensional material balance equation

$$\frac{\partial c_i}{\partial t} = \frac{D_i}{\delta_y^2} \frac{\partial^2 c_i}{\partial y^2} + 3 \frac{D_{b,i}}{\delta_y^2} \frac{\partial c_i}{\partial y} + \frac{z_i F D_i}{\delta_y RT} \left( \frac{\partial \Phi}{\delta_y} \frac{\partial c_i}{\partial y} + c_i \delta_y \frac{\partial \Phi}{\partial y} \right) + R_i$$  \[15\]

where $R_i$ has been defined previously. The dimensionless distance is defined as

$$\xi = y/\delta_y$$  \[16\]

where $y$ is the normal distance from the electrode surface, and $\delta_y$ is the diffusion layer thickness which is related to the rotation speed of the electrode by the relation (18)

$$\delta_y = \left( \frac{3 \alpha_\text{D}}{\nu \Omega} \right)^{1/2}$$  \[17\]

The initial conditions are

$$\text{at } t = 0 \text{ and } \xi \geq 0 \quad c_i = c_{i,\text{bulk}} \text{ and } \Phi = \Phi_\text{m}$$  \[18\]

and the boundary conditions are as follows

$$\text{at } \xi = 2 \text{ and } i > 0 \quad c_i = c_{i,\text{bulk}} \text{ and } \Phi = \Phi_\text{e}$$  \[19\]

where $c_{i,\text{bulk}}$ is assumed to be equal to $c_{i,\text{ref}}$ at the electrode surface

$$\text{for } t > 0 \text{, as } \xi \to 0, \Phi \to \Phi_\text{e} \text{ and }$$

$$\frac{1}{\delta_y} \int_{-\delta_y}^{\delta_y} \left( D_i \frac{\partial c_i}{\partial y} + z_i F D_i \frac{\partial \Phi}{\partial y} \right) dy = \sum_j s_{ij} j_j$$  \[20\]

Steady-state results are obtained by equating the left-hand side of Eq. [13] to zero, that is

$$\frac{\partial c_i}{\partial t} = 0$$  \[21\]

The bulk concentration of dissolved O$_2$ and CO$_2$ in the melt is determined by Henry’s law

$$c_i = H_i \rho_i$$  \[22\]

where the bulk concentrations of O$_2$ and O$_{\text{red}}$ species formed by the chemical dissolution of O$_2$ in the melt are determined by the equilibrium relations established in Eq. [8] and [9] (5, 6). The bulk concentration of O$_{\text{red}}$ species is calculated from Eq. [6] under equilibrium conditions.

Thermodynamic information on the standard electrode potentials for the electrochemical reactions and the equilibrium constants for the chemical reactions were obtained from the free energy calculations for these reactions. The electrode potential of the reference oxygen electrode (35% O$_2$:65% CO$_2$ mixture) at 750°C in various carbonate melts was calculated from the free energies of formation (19). The free energy changes (and therefore the equilibrium constants) of the reactions

$$\text{M}_2\text{O} + 1/2 \text{O}_2 = \text{M}_2\text{O}_2$$  \[23\]

$$\text{M}_2\text{O} + 2 \text{O}_2 = 2 \text{MO}_2$$  \[24\]

$$1/2 \text{M}_2\text{O} + 3/4 \text{O}_2 = \text{MO}_2$$  \[25\]

$$2/3 \text{M}_2\text{O} + 2/3 \text{MO}_2 = 2/3 \text{MO}_2 + 1/3 \text{O}_2$$  \[26\]

(where M stands for Li, K, or Na) were calculated using the free energy data from the JANAF tables (19) (assuming the ideal mixing rule). Next, the standard electrode potentials for the electrochemical reactions were calculated with respect to the reference oxygen electrode in the same melt. The free energies of MO$_2$, M$_2$O$_2$, and MO in the liquid state are not available and therefore, the solid-state values were used as an approximation. The free energy of formation of LiO$_2$ is also not available. It was estimated from the solubility data of oxygen in fused Li/K carbonate (20) as $-184.87$ KJ/mol at 1023.15 K. The validity of this value was checked by applying the fact that if a ternary compound lies on a known pseudo-binary tie line within a ternary system, it could be possible to extract that compound’s minimum or maximum allowable free energy from the free energies of the two other compounds lying along the same pseudo-binary tie line (21). From Eq. [23] and [25], with M = Li, the maximum and minimum allowable free energies of formation were estimated as $-158.23$ and $-207.16$ KJ/mol. The estimated value of $-184.87$ KJ/mol lies within this range.

The solution of the model equations was carried out by casting the governing equations in the finite difference form and solving the resulting algebraic equations by Newman’s technique (21). The solution yields the potential and the concentration profiles of reacting species in the diffusion layer, and the partial current densities at the electrode surface.

**Results and Discussion**

Table I lists the thermodynamic and kinetic parameter values used in the simulation. Figure 1 shows a plot of
Table I. Thermodynamic properties and kinetic parameters for model simulation

<table>
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<tr>
<td></td>
<td>( K_1 \times 10^{16} ) (atm)</td>
<td>19.65</td>
<td>5.22</td>
<td>0.007</td>
<td>0.014</td>
<td>55.04</td>
<td>11,500</td>
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<td>( K_2 \times 10^6 ) (mol/cm²/atm)</td>
<td>3.40</td>
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<td>3.53</td>
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<td>( K_4 \times 10^{14} )</td>
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<td>701</td>
<td>329</td>
<td>0.11</td>
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<td>( U_0 ) (V)</td>
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<td>1.58</td>
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<td>( \alpha_0 )</td>
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<td>( \alpha_4 )</td>
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<td>( t_0 ) (mA/cm²)</td>
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<td>( n_1 )</td>
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<td>1</td>
<td>1</td>
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<td></td>
<td>( D_1 \times 10^4 ) (cm²/s)</td>
<td>1.10</td>
<td>1.31</td>
<td>1.20</td>
<td>0.91</td>
<td>1.10</td>
<td>1.12</td>
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<td>( D_2 \times 10^5 ) (cm²/s)</td>
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<td>0.99</td>
<td>1.20</td>
<td>0.91</td>
<td>1.10</td>
<td>1.12</td>
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<tr>
<td></td>
<td>( H_1 \times 10^5 ) (mol/cm³/atm)</td>
<td>--</td>
<td>117</td>
<td>2.23</td>
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<td></td>
<td>( v ) = 0.011 cm²/s, ( T = 1023 ) K, ( \Omega = 1600 ) rpm, ( \rho_0 = 1.96 ) g/cm³</td>
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Table II. Solution properties

<table>
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<tr>
<th>Species</th>
<th>( D_1 \times 10^4 ) (cm²/s)</th>
<th>( D_2 \times 10^5 ) (cm²/s)</th>
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<td>Li⁺</td>
<td>1.10</td>
<td>1.20</td>
</tr>
<tr>
<td>K⁺</td>
<td>1.31</td>
<td>0.91</td>
</tr>
<tr>
<td>Na⁺</td>
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<td>0.91</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.91</td>
<td>1.20</td>
</tr>
<tr>
<td>O₂</td>
<td>1.10</td>
<td>1.12</td>
</tr>
</tbody>
</table>

The current density vs. the applied potential in the steady state, in the absence of dissolved molecular \( O_2 \) in the diffusion layer region. The contribution to the total current due to the reduction of \( O_2 \) and \( O_2 \) species in the melt is reflected in the partial current density plots in Fig. 1. The dashed curve represents the \( 2e^- \) reduction of \( O_2 \) species and the dotted curve represents the \( 1e^- \) reduction of \( O_2 \) species. The net current density (the solid line) is the sum of the two reactions, which is the same as the \( 3e^- \) reduction of \( O_2 \) to \( O^- \). The current density due to the reduction of \( O_2 \) by reaction [4] in the limiting region is about twice that due to the reduction of \( O_2 \) by the \( 1e^- \) process in reaction [3]. The predominant diffusing species in this melt calculated from the equilibrium relations established in Eq. [1] and [2] is the \( O_2 \) species. Assuming the diffusion coefficient for \( O_2 \) to be the same as that for \( O_2 \) ions, then one would expect the limiting current density of reaction [3] to be greater than that for reaction [4]. However, the reverse situation occurs in this case, as confirmed by the partial current density plots in Fig. 1. This suggests that either \( O_2 \) is acting as a reservoir for \( O_2 \) species or the product \( O_2 \) species of reaction [3] reacts further at more negative potentials to enhance the limiting current of the peroxide reaction. It is likely that both processes might be taking place. Appleby and Nicholson (3, 4) concluded from the analysis of potential scan results in Na/K melt that the \( O_2 \) species produced by the partial reduction of \( O_2 \) ions in Eq. [3] are not reduced further to \( O^- \) because of the accumulation of the latter species in the vicinity of the electrode, with consequent shift in the local electrode potential. The accumulation of \( O^- \) ions in the vicinity of the electrode in this melt was attributed to the slow neutralization reaction in Eq. [6]. While this seems to be the case under unsteady-state conditions, in the steady state there is sufficient time for neutralization to take place at least in Li/K melt.

The experimental results of Vogel et al. (6) suggest that reduction of \( O_2 \) in 62:38 Li/K carbonate melt occurs predominantly by the reduction of \( O_2 \) ions in a single wave. These authors interpreted their results (6) in terms of a complete reduction of \( O_2 \) ions by a \( 3e^- \) process in a single wave, corresponding to the solid curve in Fig. 1. However, the likelihood of \( O_2 \) species being reduced by a \( 3e^- \) process in a single step is remote. Therefore, a multi-step electrode process such as that outlined in this work (reactions [3] and [4]) is more appropriate.

The presence of dissolved molecular \( O_2 \) outside the diffusion layer region of the melt, corresponding to a possible porous electrode model, significantly enhances the cathodic currents particularly in the mass-transfer limiting region. In Fig. 2, the ratio of the limiting current in the presence and absence of simulated dissolved molecular oxygen for the electrode reactions in Eq. [3] and [4], respectively, is approximately the same. This indicates that physically dissolved oxygen in the melt influences the reduction of both \( O_2 \) and \( O_2 \) species to the same extent. Figure 3...
shows the steady-state current density change as the simulated Henry's law constant for oxygen is allowed to vary outside of the diffusion region. The higher the concentration of dioxygen outside of the diffusion layer region, the greater the reduction current. The observed enhancement in reduction currents with increase in the partial pressure of oxygen above the melt (4, 10, 22) is attributed to the effect of chemical dissolution of oxygen. On the other hand, a comparison between shielded and unshielded working electrodes has shown that the enhancement of the reduction current can be attributed to a direct reduction of oxygen through the meniscus/film on the unsheathed electrode (22). These results emphasize the significance of physically dissolved, unreacted oxygen in the diffusion layer region of the melt, which may be particularly important in porous electrodes.

Figure 4 shows a plot of predicted values of log current density vs. the concentration of the dissolved gases (O₂ and CO₂) in the near-reversible (Eₜₚₚ = -0.2V) and mass-transfer limiting regions (Eₜₚₚ = -1.00V). The slopes of the lines for oxygen are +0.39 in the near-reversible region and +0.14 in the mass-transfer limiting region. The small positive reaction order with respect to oxygen is in agreement with some experimental results in carbonate melts (3, 10); however, it should be noted that the claim that the slope is +0.27 and -0.12 is shown for CO₂ in the near-equilibrium and mass-transfer limiting regions.

Reaction orders of +0.27 and -0.12 are shown for CO₂ in the near-reversible region as the concentration of dissolved CO₂ in the melt increases. However, in the mass-transfer controlled region, the limiting current density decreases with a rise in the concentration of dissolved CO₂. The opposite effect is observed when the CO₂ concentration in the melt decreases. Lu (10) reported that feed gases with low CO₂ or low O₂ content will tend to cause high over-potentials at the cathode. This observation is in agreement with the results in Fig. 5. The simulated polarization curves in the presence of dissolved CO₂ can be explained by increasing the neutralization rate of oxide ions according to reaction [6] as CO₂ concentration is allowed to increase. The neutralization of oxide ions decreases the basicity of the melt and results in a shift of the reduction potential of reaction [4] to more anodic potentials. This facilitates the reduction of O₂ ions, in particular the peroxide product of reaction [3], giving higher current densities. At low concentrations of CO₂ in the melt, the neutralization of oxide ions is slow, which causes a displacement of the local reduction potential of peroxide ions to more negative potentials. As a result, the peroxide product of reaction [5] is not further reduced, leading to lower current densities.

In the mass-transfer control region, the neutralization reaction exerts less influence on the limiting currents. The limiting current densities then depend predominantly on the bulk concentration of O₂ and O₃ ions in the melt. From the equilibrium expressions in Eq. [8] and [9], these concentrations depend negatively on the partial pressure of CO₂. Therefore, high CO₂ concentrations result in lower limiting currents, whereas low CO₂ concentrations result in higher limiting currents.

The simulated effect of changes in the autocatalytic reaction rate (i.e., enhancement of dioxygen concentration unneutralized as O²⁻ increases in the presence of molecular oxygen) on the polarization curves is shown in Fig. 6 by allowing the molecular concentration outside of the diffusion layer to vary, simulating the porous electrode case. The enhancement in current density is particularly promi-
ment in the mass-transfer limiting region, and less so in the near-reversible region. High rates of the autocatalytic reaction, Eq. [5], favor the consumption of $O_2$ ions and the formation of $O^-$ ions in the melt. The $O_2$ from reaction [5] is reduced in reaction [3], thus enhancing the current density. On the other hand, a consumption of oxide ions in reaction [5] results in a lowering of the local reduction potential for peroxide in Eq. [4], so that the increased amount of $O_2$ formed via reaction [3] is further reduced in reaction [4], giving an increase in current density. The overall effect is a significant enhancement of the current density at high rates via the autocatalytic reaction, which should be important in porous electrodes.

Figure 7 shows the effect of varying the rate of the oxide neutralization reaction on the polarization curves. These are characterized at high neutralization rate constant values by a current density enhancement in the kinetic control region and a corresponding decrease in the mass-transfer control region. The reverse situation would be observed at low neutralization rate constant values. Hence, if the neutralization reaction is slow and possibly rate-determining, overpotential in the kinetic control region will be considerable. As expected, the effect of the neutralization rate constant on the polarization curves is similar to that of $O_2$ concentration. However, there is less variation in the overall range of current density in this case than would be expected if the concentration of $CO_2$ is allowed to vary.

The simulated polarization curves in various carbonate mixtures (Fig. 8 and 9) illustrate the effect of the cations present in the melt. The partial pressures of $O_2/CO_2$ are assumed to be the same level for all melt compositions. As a first-order estimate, the kinetic parameters were assumed to be the same for each melt except in Li2CO3 where only $O_2$ is the dissolved dioxygen ion. Figure 8 shows the case where dissolved molecular $O_2$ is negligible outside of the diffusion layer region, whereas Fig. 9 corresponds to the case where dissolved molecular $O_2$ is present. Both groups of polarization curves are similar; the major difference is the expected enhancement of the current densities for the latter case. The curves indicate that polarization of the MCFC cathode is dependent on the melt composition. As expected, the polarization curve in Li2CO3 shows only one limiting current, whereas those for other melts appear to show two limiting current regions; the first occurs near the open-circuit potential and corresponds to the reduction of $O_2$ species, the second occurs in the more cathodic potential region corresponding to the reduction of $O_2$. The first limiting current is not well defined in most cases and overlaps the second limiting current, as in the Li/K melt. However, two distinct limiting current regions can be observed in Na/K carbonate melts, in agreement with the results of Appleby and Nicholson in Li/K, Na/K, and Li carbonate melts (2-4).

Thermodynamic calculations indicate the equilibrium concentration of $O_2$ is in the order $K > Na > Li$, whereas the concentration of $O_2$ is the reverse. Thus, K- or Na-rich melts produce the highest concentration of $O_2$. It is apparent that the higher the concentration of $O_2$ in the melt, the higher is the limiting current density. Consequently, the Li2CO3 melt, where only $O_2$ is present, will show the lowest limiting current density. Thermodynamic calculations also indicate that reduction of $O_2$ ions occurs at more anodic potentials than that for $O_2$. Hence, kinetics near the reversible potential area are more dependent on $O_2$ ion concentration. Examination of the simulated polarization curves in Fig. 8 and 9 indicate that Li/K, Li/Na/K, Li/Na, and pure Li (Li-rich) melts should yield the best kinetic performance (lower overpotentials) in this region, where fuel cells normally operate.

Figures 10 and 11 show the effect of changing cation composition on the polarization curve in Li/K melts. In general, the electrolyte composition exhibits the same behavior in the presence or absence of dissolved oxygen outside of the diffusion layer region. Improved kinetics in the
near-reversible are observed with increasing Li-content, whereas the limiting currents do not vary significantly. These results are in general agreement with one set of fuel cell performance data results for melts of various compositions (23), however other analyses show discrepant results.

Finally, a sensitivity analysis similar to that reported earlier (24) was carried out for this system. The most sensitive parameters were found to be the apparent transfer coefficients, followed by the exchange current densities and the reaction rate constants; the least sensitive parameters were the diffusion coefficients of reacting species.

Conclusions
Mathematical modeling shows that the polarization curves for oxygen reduction in carbonate melts should be significantly affected by the concentrations of dissolved CO₂ and O₂ outside of the diffusion layer in the melt as well as by changes in the rates of the autocatalytic (O₂ + 2 O₂ → 2 O₃) and neutralization (CO₂ + O₂ → O₃ + O₂) reactions. Simulation for different cation mixtures indicates that melts with high Li-content should yield the highest kinetic rates. At present, experimental observations for comparison with the model simulations in this work are generally lacking. It is hoped that experiments on microelectrodes and ultrathin porous electrodes in various carbonate melts currently in progress in the authors' laboratory will lend support to the conclusions drawn from this work.

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APPENDIX
Derivation of Kinetic Expression for the Electrode Reactions
The kinetic rate equations for reactions [3] and [4] are derived separately and then combined to obtain the overall rate equation at the electrode. For example, to derive the rate equation for reaction [4], the reaction is assumed to proceed by a sequence of elementary steps as outlined below

\[ \text{O}_2^- + e^- \rightleftharpoons \text{O}^2^- + \text{O}^- \]  \hspace{1cm} [4a]
\[ \text{O}^- + e^- \rightleftharpoons \text{O}^0 \]  \hspace{1cm} [4b]
\[ \text{O}^0 + 2e^- \rightleftharpoons 2 \text{O}^- \]  \hspace{1cm} [4]

where Eq. [3a] is taken to be the rate-determining step (rds). The following assumptions were made to facilitate the derivation of the kinetic expression for the current density; (i) the rates of the elementary steps prior to and after the rds are high enough to be in quasi-equilibrium; (ii) the coverage of the electrode surface by adsorbed species is low; (iii) double layer effects are negligible, and (iv) the electrolyte behaves as an ideal solution.

The rate expression for the rds in Eq. [4a] can be expressed by the equation

\[ \frac{i_{4a}}{n_{4a}F} = k_{4a}c_{\text{O}_2}c_{\text{O}^-} \exp \left( \frac{\beta F}{RT} V \right) - k_{-4a}c_{\text{O}_2} \exp \left( - \frac{1 - \beta F}{RT} V \right) \]  \hspace{1cm} [A-1]

where \( V \) is the potential difference between the electrode and the adjacent solution

\[ V = \phi_{\text{net}} - \phi_a \]  \hspace{1cm} [A-2]

Application of the quasi-equilibrium assumption to Eq. [4b] gives rise to the following expressions

\[ K_{4b} = \frac{k_{4b}}{k_{-4b}} = \frac{c_{\text{O}^-}}{c_{\text{O}^0}} \exp \left( - \frac{F}{RT} V \right) \]  \hspace{1cm} [A-3]

which is substituted into Eq. [A-2] for \( \phi_a \) to give

\[ i_{4a} = k_{4a}c_{\text{O}_2} \exp \left( \frac{\alpha_{4a}F}{RT} V \right) - k_{-4a}c_{\text{O}_2} \exp \left( - \frac{\alpha_{4a}F}{RT} V \right) \]  \hspace{1cm} [A-4]

where \( k_4 = n_{4a}k_{4a}K_{4b} \) and \( k_{-4} = n_{4a}k_{-4a}K_{4b} \) and where \( \alpha_{4a} = 1 + \beta \) and \( \alpha_{-4a} = 1 - \beta \). It must be noted that

\[ \alpha_{4a} + \alpha_{-4a} = n_a = 2 \]  \hspace{1cm} [A-5]

where \( n_a \) is the total number of electrons transferred in reaction [4]. At equilibrium, \( i_4 = 0 \) and the potential \( V \) becomes equal to the Nernst or equilibrium potential, \( V_{\text{eq}} \).

That is

\[ i_4 = 0 = k_{4a}c_{\text{O}_2} \exp \left( \frac{\alpha_{4a}F}{RT} V_{\text{eq}} \right) - k_{-4a}c_{\text{O}_2} \exp \left( - \frac{\alpha_{4a}F}{RT} V_{\text{eq}} \right) \]  \hspace{1cm} [A-6]

The exchange current density corresponding to this surface equilibrium composition, \( i_{4a}^\infty \), is defined as

\[ i_{4a}^\infty = k_{4a}c_{\text{O}_2} \exp \left( \frac{\alpha_{4a}F}{RT} V_{\text{eq}} \right) - k_{-4a}c_{\text{O}_2} \exp \left( - \frac{\alpha_{4a}F}{RT} V_{\text{eq}} \right) \]  \hspace{1cm} [A-7]


\[ \frac{i_4}{i_{4a}^\infty} = \exp \left[ \frac{\alpha_{4a}F}{RT} (V - V_{\text{eq}}) \right] - \exp \left[ - \frac{\alpha_{4a}F}{RT} (V - V_{\text{eq}}) \right] \]  \hspace{1cm} [A-8]
In terms of reaction [4], the open-circuit potential is given as

$$U_{\text{ref}} = \frac{\alpha_i F}{n_4} \ln \left( \frac{C_{o4,\text{ref}}}{C_{o4}} \right)$$  \hspace{1cm} \text{[A-10]}

The equilibrium relation from Eq. [1] in Li-K melt is given as (5)

$$C_{o4,\text{ref}} = K_l \frac{p_{04}^{2/3}}{p_{O_2,\text{ref}}}$$  \hspace{1cm} \text{[A-11]}

and from Eq. [6] under equilibrium conditions

$$C_{O_2,\text{ref}} = K_{02} p_{O_2,\text{ref}}$$  \hspace{1cm} \text{[A-12]}

Therefore the exchange current density can be expressed in terms of the partial pressures of $O_2$ and $CO_2$ as follows

$$i_{4,\text{ref}} = \frac{k_{4}^{\alpha_t \approx 0} p_{O_2}^{2/3}}{K_{02} p_{O_2,\text{ref}}} \frac{p_{CO_2,\text{ref}}^{-1/2}}{p_{04}^{1/2}}$$  \hspace{1cm} \text{[A-13]}

The open-circuit potential for reaction [4] evaluated at the reference electrode, $U_{4,\text{ref}}$, as expressed below

$$U_{4,\text{ref}} = \frac{\alpha_i F}{n_4} \ln \left( \frac{C_{o4,\text{ref}}}{C_{o4}} \right)$$  \hspace{1cm} \text{[A-20]}

where

$$i_4 = \frac{k_{4}^{\alpha_t \approx 0} p_{O_2}^{2/3}}{K_{02} p_{O_2,\text{ref}}} \frac{p_{CO_2,\text{ref}}^{-1/2}}{p_{04}^{1/2}}$$  \hspace{1cm} \text{[A-24]}

Equation [A-2] is substituted for $V$ in Eq. [A-20] and the result is substituted into Eq. [A-14]. With further simplification and rearrangement, the final expression for the current density is

$$i_4 = \frac{k_{4}^{\alpha_t \approx 0} p_{O_2}^{2/3}}{K_{02} p_{O_2,\text{ref}}} \frac{p_{CO_2,\text{ref}}^{-1/2}}{p_{04}^{1/2}}$$  \hspace{1cm} \text{[A-22]}

and the exchange current density with respect to the partial pressures of $O_2$ and $CO_2$ is given by

$$i_{4,\text{ref}} = \frac{k_{4}^{\alpha_t \approx 0} p_{O_2}^{2/3}}{K_{02} p_{O_2,\text{ref}}} \frac{p_{CO_2,\text{ref}}^{-1/2}}{p_{04}^{1/2}}$$  \hspace{1cm} \text{[A-25]}

Experimentally, the measured potential is generally referred to as the applied potential, $E_{\text{app}}$, and is the potential difference between working electrode, $\Phi_{\text{ww}}$, and the potential at the reference electrode, $\Phi_{\text{ref}}$, as expressed below

$$E_{\text{app}} = \Phi_{\text{ww}} - \Phi_{\text{ref}}$$  \hspace{1cm} \text{[A-27]}

where

$$\eta_i = \Phi_{\text{ref}} - \Phi_{\text{oo}} - U_{4,\text{ref}}$$  \hspace{1cm} \text{[A-28]}

where $\Phi_{\text{oo}}$ is the ohmic potential drop in the solution. Consequently, the measured overpotential is

$$\eta_i = \Phi_{\text{ref}} - \Phi_{\text{oo}} - U_{\text{exp}}$$  \hspace{1cm} \text{[A-29]}

where $U_{\text{exp}}$ is the open-circuit potential.

**LIST OF SYMBOLS**

- $c_i$: concentration of species $i$, mol/cm$^3$
- $D_i$: diffusion coefficient of species $i$, cm$^2$/s
- $D_{R}$: diffusion coefficient of limiting reactant, cm$^2$/s
- $E_{\text{app}}$: applied electrode potential, V
- $F$: Faraday constant, 96,487 C/mol
- $H$: Henry’s constant for species $i$
- $i$: local current density due to reaction $j$, A/cm$^2$
- $i_{0j}$: exchange current density due to reaction $j$ at surface concentrations, A/cm$^2$
- $i_{0j,\text{ref}}$: exchange current density due to reaction $j$ at reference concentrations, A/cm$^2$
- $i_{\text{total}}$: total current density, A/cm$^2$
- $K_j$: equilibrium constant for homogeneous reaction $j$ in the bulk solution
- $k_{fj}$: forward rate constant for homogeneous reaction $j$
- $k_{rj}$: backward rate constant for homogeneous reaction $j$
- $k_{f}\text{}_{j}$: forward rate constant for reaction $j$ on the electrode
- $k_{r}\text{}_{j}$: backward rate constant for reaction $j$ on the electrode
- $N_i$: number of species in the solution
- $N_{j}$: number of electrons transferred in reaction $j$
- $P_{i}$: partial pressure of component $i$ in gas mixture, atm.
- $R$: universal gas constant, 8.314 J/mol-K
- $R_{p}$: rate of disappearance of species $i$ by a homogeneous reaction in the solution, mol/s
- $rpm$: revolution per minute
- $s_i$: stoichiometric coefficient of species $i$ in reaction $j$
- $T$: absolute temperature, K
- $u_i$: mobility of species $i$, cm$^2$/mol-s
- $V_{\text{o}_2}$: theoretical open-circuit potential for reaction $j$, V
- $V_{\text{exp}}$: standard electrode potential for reaction $j$, V
- $V_{\text{exp}}$: open-circuit potential with respect to the reference $O_2$ electrode
Analysis of a Pulsed-Plasma Chemical Vapor Deposition Reactor with Recycle

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ABSTRACT

A simplified model for a time-dependent plasma-assisted chemical vapor deposition reactor was developed based on transport and reaction principles. The model equations were solved by the method of lines using collocation on finite elements for the spatial discretization. Emphasis was placed on the deposition rate and uniformity as a function of reactor operating conditions. A pulsed-plasma reactor was analyzed and compared to a continuous-wave (CW) plasma reactor. Under conditions which would result in high depletion of the precursor gas in the CW reactor, the pulsed-plasma reactor yielded improved uniformity, albeit the deposition rate was reduced. The effect of a recycle stream on both the CW and pulsed-plasma reactors was also studied. For the CW reactor, recycle was most beneficial under conditions of low depletion of the precursor gas. For cases of intermediate depletion of the precursor gas, a CW reactor with recycle or a combination of pulsed-plasma and recycle can result in nearly uniform deposit without sacrificing the deposition rate. Analytic solutions were derived for the CW reactor with recycle, and for a well-mixed pulsed-plasma reactor. The results apply equally well to pulsed-plasma etching reactors conforming to the model assumptions and operating under corresponding conditions.

Plasma-assisted deposition and etching of thin solid films has emerged as a crucial step in the fabrication of microelectronic components (1), and is expected to become even more important in the future. In plasma processing, a low-pressure gas discharge is used to decompose an otherwise inert gas to produce reactive atoms and radicals. The reactive species interact with a substrate to deposit a thin film or to etch the substrate by forming volatile products (2).

Plasma-assisted chemical vapor deposition (PCVD) is used extensively to grow a variety of thin films including dielectrics (e.g., SiO2, and Si3N4) (3, 4), amorphous hydrogenated silicon a-Si:H (5), polymers (6), and more recently diamond (7). In particular, PCVD is the method of choice when low-temperature deposition is required. For example, PCVD is used to deposit a Si3N4 passivation layer over devices in which aluminum metallization prohibits the use of conventional high-temperature CVD methods.

Important goals of PCVD include high deposition rate and uniformity, and high quality of the deposited film.

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U°n standard potential of the reference electrode on the absolute thermodynamic scale, V
V potential difference between metal of the working electrode and the solution just outside the diffuse double layer, V
V°,j value of V when working electrode is at equilibrium
v bulk fluid velocity, cm/s
y normal coordinate into the solution from the electrode surface, cm
z_i charge of species i
Greek
α_j an apparent anodic transfer coefficient for reaction j
β_j apparent cathodic transfer coefficient for reaction j
δD diffusion layer thickness, cm
ρ_s density of solution, kg/cm^3
η_j overpotential of reaction j, V
μ_i stoichiometric coefficient of species i in a homogeneous reaction
ν kinematic viscosity, cm^2/s
ξ dimensionless distance, y/v
Ω rotation speed, rad/s
Subscripts
o at the electrode surface
j reaction, j
re reference electrode
ref reference conditions
bulk in the bulk solution