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Oxygen Electrode Reaction in Molten Carbonate Fuel Cells

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OXYGEN REDUCTION IN LITHIUM CARBONATE
MELT: DETERMINATION OF ELECTRODE
KINETIC AND MASS TRANSFER PARAMETERS

A Dissertation

by

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ABSTRACT

Oxygen Reduction in Lithium Carbonate Melt: Determination
of Electrode Kinetic and Mass Transfer Parameters. (May 1991)

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Molten carbonate fuel cell system is a leading candidate for the utility power generation because of its high efficiency for fuel to AC power conversion, capability for an internal reforming, and a very low environmental impact. However, the performance of the molten carbonate fuel cell is limited by the oxygen reduction reaction and the cell life time is limited by the stability of the cathode material. An elucidation of oxygen reduction reaction in molten alkali carbonate is essential because overpotential losses in the molten carbonate fuel cell are considerably greater at the oxygen cathode than at the fuel anode. The oxygen reduction reaction in molten alkali carbonate electrolyte is complex and does not directly involve molecular oxygen. The oxygen reduction mechanism strongly depends on the cations present in the melt.

Oxygen reduction on a fully immersed gold electrode in a lithium carbonate melt was investigated by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) to determine electrode kinetic and mass transfer parameters. The impedance spectra were analyzed using the Randles-Ershler equivalent circuit model and a computer Nonlinear Least Square (CNLS) program to determine parameters such as the charge transfer resistance, Warburg coefficient, double layer capacity, and uncompensated electrolyte resistance. Cyclic voltammetric measurements showed that oxygen reduction in a pure lithium carbonate melt is very rapid. The invariance of peak potential with respect to the scan rate and linear behavior of the peak current density with respect to square root of the scan rate indicated that the oxygen reduction in a pure lithium carbonate melt is "reversible" up to 200 mV/s.

The dependences of electrode kinetic and mass transfer parameters on gas composition and temperature were examined to determine the reaction orders and the activation energies. The results showed that oxygen reduction in a pure lithium carbonate melt occurs via the peroxide mechanism. A mass transfer parameter, $D_O^{1/2}C_O$, estimated by the cyclic voltammetry concurred with that calculated by the EIS technique. The temperature dependence of the exchange current density and the product $D_O^{1/2}C_O$ were examined and the apparent activation energies were determined to be about 122 and 175 kJ/mol, respectively.

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To
My Mother, Triguna Davé
and
My Wife, Sandra Burke

For Their Unwavering Love, Patience, and Sacrifice

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CHAPTER I

INTRODUCTION

A fuel cell is an electrochemical device that converts the free energy of the reactants (fuel and oxidant) directly and continuously into electrical energy. The energy conversion efficiency of a thermal power plant is limited by the highest temperature used in the cycle (i.e., Carnot cycle efficiency). Whereas theoretically, fuel cells can convert all the free energy available from fuel oxidation reaction into electrical energy. In reality, the energy conversion efficiency of a fuel cell is less than 100% because of the losses due to irreversibility of the process. Fuel cells have many advantages over the conventional energy conversion technologies such as the thermal power plants (1): i) high energy conversion efficiency; ii) efficiency relatively independent of load; iii) modular design makes an efficiency of a fuel cell power plant independent of plant scale; iv) very low environmental impact due to reduced chemical and acoustic pollution; v) fast reactive power; and vi) multi-fuel ability.

Although Sir Humphrey Davy suggested the fuel cell reactions in 1802, the first successful fuel cell was operated by Sir William Grove (2) in 1839. Grove used hydrogen and oxygen in his "Gaseous Voltaic Battery" to produce electricity and water. Grove's work was corroborated by Mond and Langer (3) who also found the necessity of preventing the flooding of the platinum black electrode by using a porous, nonconducting substance to contain the electrolyte. The renaissance of fuel cells began in 1950s when Bacon (4) introduced a fuel cell with dual porosity electrodes made of nickel and lithiated nickel oxide; modern version of this fuel cell is now used as a power source in the space shuttle.

Types of Fuel Cells

Since the first fuel cell invented by Sir William Grove, many different types of fuel cell are invented. At present, the cells operate from room temperature of 25°C to 1000°C.

This dissertation follows the style of the Journal of the Electrochemical Society.

and use variety of fuels such as gaseous hydrogen, alcohols, natural gas, and gasified coal. The fuel cells classified by the electrolytes are as follows: (i) alkaline fuel cell, (ii) proton exchange membrane fuel cell, (iii) phosphoric acid fuel cell, (iv) molten carbonate fuel cell, and (v) solid oxide fuel cell. The alkaline and proton exchange membrane fuel cells operate at low temperatures and their main application is in space. These fuel cells also have very good potential for terrestrial transportation (e.g., electric vehicles). The other fuel cells operate at higher temperatures and the principal applications are utility power generation, dispersed power generation, and industrial cogeneration.

Alkaline Fuel Cell

The alkaline fuel cell (AFC) operates at about 60°C to 80°C temperature and contains concentrated KOH (~45 wt%) to lower the vapor pressure of water. The ionic current through the electrolyte is carried by OH^- ions. The main advantage of an alkaline electrolyte is that inexpensive electrocatalysts can be used for oxygen reduction reaction. The porous electrodes made of Raney nickel or PTFE-bonded catalyzed carbon may be used in AFC. The major limitation of the AFC is that high purity of hydrogen and oxygen is required. Since, the AFC does not reject carbon dioxide, fuel gas derived from the carbonaceous fuel is unsuitable.

Proton Exchange Membrane Fuel cell

The Proton Exchange Membrane Fuel cell (PEMFC) consists of a solid polymeric electrolyte (e.g., perfluorosulfonic acid membrane) sandwiched between two platinum catalyzed, PTFE-bonded carbon electrodes. The ionic conductivity of the electrolyte is due to the transport of proton. The PEMFC is a high power density fuel cell which operates at about 80°C. Since the proton exchange membrane is non-corrosive, corrosion problems for PEMFC are minimal. Some of the disadvantages of PEMFC are that it requires high-cost membrane and Pt catalyst, CO is an anode poison (i.e., reformate gas is not suitable), and water management is very crucial for the efficient performance.

Phosphoric Acid Fuel Cell

The phosphoric acid fuel cell (PAFC) operates between 100 and 200°C temperature. The porous electrodes consist of carbon supported Pt catalysts bonded with PTFE on a substrate made of carbon. The PAFC is the most advanced fuel cell system for terrestrial power generation. The PAFC has a very high overall fuel efficiency for on-site cogeneration application because the operating temperature is high enough to produce steam. Also, the phosphoric acid is a CO₂-rejecting electrolyte. But oxygen reduction in acid electrolyte is sluggish and requires expensive, noble metals as electrocatalysts. The carbon monoxide is an anode poison; hence hydrogen is the only suitable fuel for direct oxidation.

Molten Carbonate Fuel Cell

The molten carbonate fuel cell (MCFC) operates at about 650°C and the electrolyte consists of an eutectic mixture of lithium and potassium carbonates retained in a porous matrix made of γ -Al₂O₃. Due to its high temperature, the electrode kinetic rates are high enough that it does not require expensive electrocatalysts; moreover, high-grade waste heat can be used for internal reforming of CH₄, cogeneration, and additional generation of electric power by using a bottoming cycle. The MCFC is expected to have the highest fuel efficiency of all fuel cell systems. Some of the problems associated with MCFC are stability of cell materials, recycling of carbon dioxide, low sulfur tolerance, and high overpotential losses at the oxygen cathode. The detailed description of MCFC is given in the next section.

Solid Oxide Fuel Cell

The solid oxide fuel cell (SOFC) consists of yttria-stabilized ZrO₂ and operates at about 1000°C. The transport of oxide ions is responsible for the ionic current between the anode and the cathode. The fuel anode is made of Ni-ZrO₂ cermet (stabilized by Y₂O₃), whereas the cathode is made of Sr-doped lanthanum chromite. The SOFC has all the advantages described for MCFC. Moreover, the SOFC does not have

the problem of electrolyte management and does not require recycling of carbon dioxide. Some of the disadvantages of SOFC are high-cost fabrication process and high electrolyte resistivity.

Molten Carbonate Fuel Cell

Baur *et al.* (5) developed the first molten carbonate fuel cell, which used an equimolar mixture of sodium and potassium carbonate melt and operated at about 800-900°C. The major development of MCFC was carried out by Ketelaar and Broers (6, 7) in the Netherlands, Gorin and Recht (8, 9) in U.S.A., and Chambers and Tantram in United Kingdom (10, 11). At present Energy Research Corporation (Danbury, CT) and MC Power (Chicago, IL) are leading the molten carbonate fuel cell technology in U.S.A.

The molten carbonate fuel cell (MCFC) has many favorable characteristics for utility power generation, because it operates at about 650°C (12, 13): i) the polarization losses are reduced to such an extent that it does not require expensive catalysts as it is required in low temperature fuel cells (e.g., phosphoric acid fuel cell); ii) the operating temperature is high enough to produce high quality waste heat, yet it is sufficiently low that the decrease in the free energy is not very large (e.g., the theoretical open circuit cell voltage is 100 mV higher than that of the solid oxide fuel cell (SOFC) which operates at 1000°C); and iii) the high temperature waste heat can be used for cogeneration, a bottoming cycle and internal reforming of methane. The MCFC operates at about 650°C and 160 mA cm⁻² to produce 0.75 V per cell at atmospheric pressure and 50% fuel (hydrogen) utilization. Under pressurized conditions, the performance of MCFC would be even better.

A schematic of a single MCFC is shown in Fig.1. As the name implies, molten alkali carbonate mixture retained in a porous lithium aluminate matrix, is used as the electrolyte. At the cathode made of lithiated NiO, oxygen reacts with carbon dioxide and accepts two electrons to form carbonate ion:

The ionic current through the electrolyte matrix is carried by the carbonate ions from cathode to anode. At the nickel (with 10% Cr) anode, oxidation of hydrogen consumes the carbonate ions and forms water vapor and carbon dioxide:

releasing two electrons to the external circuit. In a practical MCFC, carbon dioxide produced at the anode need to be transferred to the cathode where it is consumed. The transfer of CO_2 from the anode exhaust to the cathode inlet can be carried out in two ways: (i) to burn the spent anode stream with excess air and mix it with the cathode inlet gas after removing the water vapor or (ii) to use a "product exchange device" to separate CO_2 from the anode exhaust (1). The latter method provides a richer oxidant since it is not diluted by nitrogen, and hence yields a higher cell voltage.

Characteristics of state of the art components of MCFC are given in Table 1. All three components of the MCFC are now manufactured using the tape casting process. The anode is made of nickel-chromium alloy (2 to 10 wt% Cr). The addition of Cr prevents the sintering of the porous anode, since it forms LiCrO_2 at the grain boundaries and prevents metal diffusion. Recently, it was found that small metal oxide (e.g. Al_2O_3 , LiAlO_2 , etc.) particles, incorporated in the anode, prevent mechanical creep. In addition to its electrocatalytic function, the anode is also required to function as an electrolyte reservoir, barrier for gas cross-over, and provide structural support the cathode and thin electrolyte matrix in the cell stack. The gas cross-over is prevented by a thin structure of fine porosity which is filled with molten carbonate electrolyte at the anode-electrolyte interface. This layer is called the bubble pressure barrier (BPB). The pore size distribution for the electrodes, electrolyte matrix, and BPB plays a very important role in establishing a stable electrolyte-gas interface in the porous electrodes since the balance in capillary pressures is used for the electrolyte distribution in the cell components. The electrolyte tile in MCFC consists of an eutectic mixture of 68% Li_2CO_3 and 32% K_2CO_3 retained in a porous $\sim\text{LiAlO}_2$ matrix. The electrolyte tile not only conducts the carbonate ions from cathode to

Fig. 1. A Schematic of a Molten Carbonate Fuel Cell.

anode but also separates the fuel and oxidant gases. The electrolyte composition is favorable, but by no means is it optimized for MCFC performance and stability. The cations present in molten alkali carbonate electrolyte has a strong effect on the performance and endurance of MCFC. High Li^+ and Na^+ contents in the electrolyte increase ionic conductivity while high K^+ promotes the gas solubility. The cathode consists of porous lithiated NiO, generally formed by *in situ* oxidation and lithiation of sintered nickel. Since lithiated NiO is a nonstoichiometric compound, $\text{Li}_x\text{Ni}_{1-x}\text{O}$ where x is in the range of 0.022-0.04, exhibits an electronic conductivity several orders of magnitude higher than that of NiO. As shown in Table 1, the typical thickness of the cathode is lower than that of the anode to lower the total electronic resistance and to obtain a better performance.

The oxygen reduction reaction occurring at the cathode is complex and depends on the cations present in the electrolyte. The oxygen reacts with the carbonate ions to form peroxide and/or superoxide ions. In a pure Li_2CO_3 or a Li-rich melt the peroxide species is dominant, whereas in a K-rich melt the superoxide is dominant. In the eutectic mixture of 68% Li_2CO_3 and 32% K_2CO_3 both peroxide and superoxide species are present (13). The electrolyte distribution is very important for the performance of cathode because it is very sensitive to the degree of filling of the pore volume by electrolyte. The optimum pore filling is about 20% and even then the overpotential losses at the cathode are considerably greater than those occurring at the anode (14). The dissolution of NiO causes a serious problem by limiting the cell life time. Although the solubility of nickel is far less than that of silver and copper (~ 10 ppm), dissolved NiO may diffuse through the electrolyte towards the anode and metallic Ni may precipitate in the regions of negative potential (i.e. the hydrogen partial pressure is sufficiently high). The deposition of metallic Ni grains in the electrolyte matrix would eventually cause the electrolyte to become electronically conducting. The rate of dissolution of NiO is proportional to the partial pressure of CO_2 and may involve the following reaction:

Table 1. Characteristics of State-of-the-Art Components for the Molten Carbonate Fuel Cell.

Component	Current Status
Anode	<ul style="list-style-type: none"> • Ni-10 wt% Cr • 3-6 μm pore size • 50-70% porosity • 0.5-1.5 mm thickness • 0.1-1 m^2/g
Cathode	<ul style="list-style-type: none"> • lithiated NiO • 7-15 μm pore size • 70-80% porosity • 0.5-0.75 mm thickness • 0.5 m^2/g
Electrolyte Support	<ul style="list-style-type: none"> • $\gamma\text{-LiAlO}_2$ • 0.1-12 m^2/g
Electrolyte ^a	<ul style="list-style-type: none"> • 62 Li-38 K • 50 Li-50 Na • 50 Li-50 K • ~50 wt%
Fabrication Process	<ul style="list-style-type: none"> • tape-cast • 0.5 mm thickness

The dissolution kinetics of NiO is also a function of basicity of the electrolyte, and hence it depends on the cations present in the melt. Research is in progress to develop alternative cathode materials and to optimize the electrolyte composition (15) to overcome the problem of cathode dissolution.

The bipolar plates in the MCFC stacks are usually fabricated from thin (~ 15 mil) sheets of an alloy (e.g. Type 310S or 316L stainless steel). The anode side of the bipolar plate is coated with Ni to prevent corrosion.

The advanced form of molten carbonate fuel cell, known as the internal reforming molten carbonate fuel cell (IRMCFC) or *direct fuel cell*, may be used to consume the lower hydrocarbons, e.g., CH₄, directly. The IRMCFC is intrinsically efficient because water vapor and heat, produced by the exothermic reaction occurring at the anode (Eqn. [2]), provide both the energy and the reactant required for the steam-reforming of methane. Since the standard nickel anode does not have sufficient activity to reform the required amount of methane to hydrogen, a supported Ni catalyst is required in IRMCFC. The IRMCFC system operating on natural gas is expected to have an overall efficiency greater than 50%.

The MCFC does not have a problem of CO poisoning of anode as in low temperature fuel cells such as phosphoric acid and proton exchange membrane fuel cells, in fact CO in the anode gas stream is used as a fuel. The fuel gas derived from fossil fuel such as coal and natural gas may contain several contaminants such as sulfur-containing compounds, particulates, trace metals etc. The performance of anode is degraded even by the small (~ 1 ppm) amounts of sulfur present in the fuel or oxidant gas stream, although the degradation is reversible. The adverse effect of S compounds on the performance of MCFC requires prior removal of the sulfur compounds from the fuel gas or periodic purging of sulfur from the system.

Used with a coal gasifier, the MCFC will yield a heat rate better than 6800 Btu/kWh or 50% efficiency for HHV coal-AC power when the high grade waste heat is used in a bottoming cycle (16). The PAFC could produce only about 9600 BTU/kWh, or 36% efficiency (17). Thus the MCFC is expected to have a better efficiency for

HHV coal-AC power using both coal-derived (18) and natural gas (19) fuels compared to that obtained by the PAFC.

Objectives

The main purpose of this work is to elucidate oxygen reduction reaction in the molten alkali carbonate electrolyte. The objectives of this research are the following: (i) design and fabrication of an electrochemical cell for high temperature electrode kinetic studies; (ii) study of oxygen reduction in a pure lithium carbonate using electrochemical impedance spectroscopic and cyclic voltammetric techniques; (iii) analysis of electrochemical impedance spectra using a Complex Nonlinear Least Square technique to determine electrode kinetic and mass transfer parameters; and (iv) determination of the activation energies and the reaction orders of the electrode kinetic parameters for oxygen reduction in a lithium carbonate melt.

Structure of Dissertation

This dissertation involves a study of oxygen electrode in the molten carbonate fuel cell. Chapter II describes the oxygen electrode reactions in molten alkali carbonate electrolytes; the reactions include (i) homogeneous chemical reactions equilibria; (ii) concept of acid-base for an electrolyte system containing oxide; and (iii) mechanism for oxygen reduction. In Chapter III, a study of oxygen reaction on a fully-submerged gold electrode in a pure lithium carbonate melt is presented. The experimental setup, and electrochemical techniques such as cyclic voltammetry and electrochemical impedance spectroscopy used to study oxygen reduction reaction are also described in Chapter III. The effects of temperature, partial pressure of oxygen, and partial pressure of carbon dioxide on oxygen reduction reaction in a pure lithium carbonate melt are described in Chapters IV, V, and VI, respectively. Chapter VII highlights the conclusions drawn from this research work and the recommendations for further investigations.

CHAPTER II

OXYGEN ELECTRODE REACTIONS IN MOLTEN ALKALI CARBONATES

Introduction

The oxygen reduction reaction in molten alkali carbonate electrolyte has been studied for the past quarter century because of its vital role in the performance of the molten carbonate fuel cell (MCFC) and the stability of the cell components. The molten electrolyte used in the MCFC may contain a mixture of alkali carbonates such as Li_2CO_3 , Na_2CO_3 , and K_2CO_3 . Currently, a eutectic mixture of 62 mol% Li_2CO_3 and 38 mol% K_2CO_3 (eutectic temperature = 488°C) is used as an electrolyte, because a high lithium content gives better cell performance. Although an eutectic mixture of $(\text{Li-K})\text{CO}_3$ is adequate, this composition is not necessarily the optimum. Several factors need to be considered to determine the optimal electrolyte composition (20): (i) ionic conductivity; (ii) solubility of reactants and products; (iii) diffusion coefficients of reactants and products; (iv) the electrode kinetics of cathodic and anodic reactions; (v) vapor pressure of the electrolyte; and (vi) stability of the cell components e.g., lithium-aluminate matrix and stainless steel current collector. The solubility of cathode made of lithiated-NiO may be the most important factor in determining the cell life time: the solubility of NiO in molten alkali is also a function of cations present in the melt. The ionic conductivity of the electrolyte increases with an increase in Li^+ and Na^+ contents while the reactant gas solubility increases with an increase in K^+ concentration (21). The vaporization of the electrolyte depends on the concentration of the hydroxyl ions which is maximum in a pure lithium carbonate melt.

Homogeneous Chemical Reactions Equilibria

The physical solubility of oxygen in molten alkali carbonate electrolytes is insignificant because oxygen reacts with the melt to form electroactive species such as superoxide and/or peroxide ions. Hence, homogeneous chemical reactions play an important role in oxygen reduction reactions in molten alkali carbonates. Andersen (22) suggested following reactions which are vital for the dependence of oxygen reduction mechanism on temperature and alkali metal composition:

The combinations of reactions [4] and [5] with [6] result in the formation of peroxide and superoxide ions, respectively:

The combination of Eqn. [4] with Eqn. [5] gives the disproportionation reaction between peroxide and superoxide species (23):

Acid-Base Relationship in Molten Alkali Carbonates

In 1923 J. N. Brønsted and T. M. Lowry proposed independently a concept of acid-base relationship that applies to aqueous as well as nonaqueous systems (24). The Brønsted-Lowry theory states that an acid is a proton donor and a base is a proton acceptor. This theory is summarized by the following equation:

The acid and base in this relation are known as a *conjugate pair*. The Brønsted-Lowry theory is actually a special case of a more general acid-base theory proposed by G.

N. Lewis which is applicable to solvents other than proton-donating ones. The Lewis theory states that an acid is a acceptor of a pair of electrons whereas a base is a donor of a pair of electrons to form a covalent bond.

Lux (25) extended the acid-base concept to molten salts containing oxide ions. Flood and Førland (26) further developed the concept, which states that an acid is an oxide ion acceptor and a base is an oxide ion donor. Similar to the Brønsted-Lowry theory, the Lewis-Flood theory for the oxide systems can be expressed as

Based on the Lux-Flood theory and Eqns. [4]-[6], oxygen and carbon dioxide are considered to be acids while peroxide, superoxide and carbonate ions are bases. The acid-base relationship defined by Lux-Flood theory is ambiguous. For example, superoxide is an acid with respect to peroxide, since superoxide ion accepts oxide ion to form peroxide:

But, according to Eqn. [5] the superoxide ion is defined as a base since it donates an oxide ion to release oxygen.

The basicity of the molten alkali carbonate electrolyte depends on the activity of the oxide ions and partial pressure of oxygen. Lu (23) suggested a function $p\text{O}^{2-}$ as a measure of the basicity of the molten carbonate containing oxide species. The function $p\text{O}^{2-}$ is similar to the concept of pH in the protogenic solvents:

$$p\text{O}^{2-} = -\log a_{\text{O}^{2-}} \quad [14]$$

The activity of oxide ions in molten alkali carbonates electrolyte depends on the dissociation process. The dissociation equilibrium is given as:

or

where, M is an alkali metal such as Li, Na, or K. The thermodynamic dissociation constant is defined as:

$$K_d = \frac{a_{O^{2-}} \cdot P_{CO_2}}{a_{CO_3^{2-}}} \quad [17]$$

Using Eqn. [17], the function pO^{2-} may be determined as a function of the dissociation equilibrium constant and partial pressure of carbon dioxide making the assumption that activity of the carbonate ions is invariant and equal to unity:

$$pO^{2-} = -\log \left(\frac{K_d}{P_{CO_2}} \right) \quad [18]$$

The values of pO^{2-} were calculated as a function of temperature and alkali metal content for 1 atm partial pressure of carbon dioxide using the thermodynamic data obtained by Andersen (22); the values are given in Table 2. As shown in Table 2, the dissociation constant decreases in several order of magnitude in the order $Li^+ > Na^+ > K^+$, i.e., for the same temperature and partial pressure of carbon dioxide, a pure lithium carbonate melt has the highest concentration of the oxide ions, while a pure potassium carbonate melt has the lowest oxide content among these melts. The dissociation constant K_d also decreases with an increase in temperature. Hence, the basicity of molten carbonate electrolyte is a function of alkali metal content, temperature, and partial pressure of carbon dioxide. The basicity of the melt increases with an increase in lithium-ion content and temperature and a decrease in partial pressure of carbon dioxide.

Oxygen Reduction in Molten Alkali Carbonate Electrolytes

The study of oxygen reduction in molten carbonates was initiated by Baur and Brunner in 1935 (27), when they studied oxygen reduction on a platinum electrode in $(Na, K)_2CO_3$ melt as a function of temperature and partial pressure of carbon dioxide. Earlier researchers studied the oxygen reduction mainly on platinum (28-33). Stepanov and Trunov studied the equilibrium potential of O_2/CO_2 on Pt (34).

Table 2. Effects of Alkali Metal Content and Temperature on the Basicity of Molten Carbonate Electrolytes at 1 atm P_{CO_2} .

Temperature °C	$p\text{O}^{2-}$		
	Li_2CO_3	Na_2CO_3	K_2CO_3
900	2.23	6.14	7.78
950	1.89	5.59	7.16
1000	1.58	5.09	6.58

and the mechanism of oxygen reduction reaction on Pt and on porous Ag (35) and concluded that the overall reaction is

Platinum is unstable in molten carbonate electrolytes (28, 36, 37) and forms complex oxide (37). Janz and Saegusa (30) showed that gold is more stable than platinum in the molten carbonate environment. The oxygen reduction on a gold electrode was also investigated by Busson *et al.* (38 - 40) and Borucka (41, 42). Borucka and Sugiyama (43, 44) conducted the kinetic studies of oxygen reduction on a $\text{O}_2/\text{CO}_2/\text{Au}$ electrode in a ternary (43.5 mol% Li : 31.5 mol% Na : 25.0 mol% K) CO_3 eutectic melt in the temperature range of 550-800°C and concluded the following: (i) the effects of the partial pressures of oxygen and carbon dioxide on the equilibrium potential show that the overall reaction at the equilibrium is represented by Eqn. [19] and the equilibrium potential obeys the corresponding Nernst equation

$$E_{\text{O}_2, \text{CO}_2 / \text{CO}_3^{2-}} = E_{\text{O}_2, \text{CO}_2 / \text{CO}_3^{2-}}^{\circ} + \frac{RT}{2F} \ln (P_{\text{O}_2}^{1/2} P_{\text{CO}_2}); \quad [20]$$

(ii) the micropolarization tests at near-equilibrium indicate that the electrode is under "mixed" control (due to the charge transfer and mass transport processes), even close to the equilibrium; and (iii) the exchange density for the electrode reaction (Eqn. [19]) is about 0.1 mA cm^{-2} . Appleby and Nicholson (45 - 49) examined the oxygen reduction reaction in molten carbonates on a submerged gold electrode using steady-state and potential-scan techniques. Appleby and Nicholson concluded that oxygen reacts with carbonate ions to form peroxide and/or superoxide ions and the concentrations of these species depend on the cations present in the melt. In a pure Li_2CO_3 or a Li-rich melt, the peroxide species is dominant, whereas in a K-rich melt the superoxide species is dominant. The existence of peroxide and/or superoxide species is also reported in the oxide-containing molten systems of fluorides (50), nitrites (51), and chlorides (52). Appleby and Nicholson also examined the oxygen reduction reaction in binary (43 mol% Na : 57 mol% K) and ternary (43.5 mol% Li : 31.5 mol% Na : 25 mol% K) eutectics in the temperature range of 700-800°C and

concluded that (47): (i) the electroactive species is not the diatomic oxygen molecule; (ii) both peroxide and superoxide ions are present; and (iii) the neutralization of the oxide ions by carbon dioxide (Eqn. [24]) is slow, and may be controlled by diffusion. Appleby and Nicholson (48) investigated the electrode kinetics of oxygen reduction on a fully-submerged gold electrode in the binary (47 mol% Li : 53 mol% K)CO₃ eutectic melt over the temperature range of 700-800°C and concluded that both peroxide and superoxide species are present in the melt, and are reduced in parallel steps. The reduction peaks for these species are closer in this melt compare to those in the binary (43 mol% Na : 57 mol% K) melt. The exchange current density values (e.g., 0.37 mA cm⁻² at 700°C and gas composition of 90% O₂ and 10% O₂) in the Li/K melt are higher than those in the Na/K melt (e.g., 0.18 mA cm⁻² at 700°C and gas composition of 90% O₂ and 10% O₂). Dunks and Stelman (53) studied the oxygen reduction in a pure sodium carbonate melt at 900°C using cyclic voltammetric and computer-curve fitting and proposed the presence of percarbonate ions. They also confirmed the existence of the superoxide ions in the frozen electrolyte from the Electron Spin Resonance (ESR) spectrum obtained at 77 K temperature. Andersen (22) carried out a thermodynamic study of the chemical equilibria in molten alkali carbonate electrolytes and determined the amount of oxide, peroxide and superoxide ions by quenching the melt followed by chemical analyses. The physical evidence of the percarbonate ions in molten carbonate is not available. The oxygen reduction mechanisms based on peroxide, superoxide, and percarbonate paths are described below:

Peroxide Path

Overall Reaction

where (O^-) is a transient species and the first charge transfer reaction (Eqn. [22]) is the rate determining step for an immersed electrode.

Superoxide Path

Overall Reaction

Percarbonate Path

Overall Reaction

The equations illustrating the dependence of the exchange current density on P_{O_2} and P_{CO_2} are derived in Appendix A. The exchange current density is related to P_{O_2} and P_{CO_2} by the following expression:

$$i_0 = i_0^0 (P_{O_2})^a (P_{CO_2})^b \quad [37]$$

where, i_0^0 is the kinetic parameter at a reference state, as indicated by super 0, and is function of temperature only, a is the reaction order with respect to oxygen, and b

is the reaction order with respect to carbon dioxide. The theoretical reaction orders for the exchange current density and the transfer coefficients determined for various reaction mechanisms are shown in Appendix A.

Tang *et al.* (54) examined the effect of gas composition on oxygen reduction kinetics on a porous NiO at 650°. The apparent exchange current density was obtained from low polarization (<10 mV) data with the assumption that the electrode reaction is under kinetic control. The kinetic reaction orders determined by Tang *et al.* are inconsistent with the theoretical mechanisms. Winnick and Ross (55) investigated the oxygen reduction kinetics on porous NiO in (Li,K)₂CO₃ eutectic melt using steady-state polarization technique. These researchers concluded that the kinetic reaction orders for oxygen and carbon dioxide are 0.25 and 0.625, respectively. These reaction orders do not concur with the any of the mechanism proposed in the literature. The discrepancy in the reaction orders determined by Tang *et al.* and Winnick and Ross may have been due to the effect of mass transfer polarization.

Appleby and Van Drunen (56) determined the total solubility of oxygen (mainly in the form of peroxide and superoxide ions) in the molten alkali carbonates as a function of temperature using the quenching method. Vogel *et al.* (57) investigated the (Li-K)CO₃ eutectic melt at 650°C, using a rotating gold wire and concluded that superoxide is dominant in this melt and presence of molecular oxygen in the melt is negligible. Smith *et al.* (58) determined the total solubility of oxygen in (Li-Na-K)CO₃ ternary eutectic melt as a function of gas composition at 650°C by a chemical method. They concluded that oxygen reacts with (Li-Na-K)CO₃ melt at 650°C to form superoxide ions and the concentration of the physically dissolved, molecular oxygen is negligible. White and Twardoch (59) examined the (Li-Na-K)CO₃ eutectic melt at 680°C by cyclic voltammetry, chronopotentiometry, and chronoamperometry and indicated the simultaneous presence of peroxide and oxide ions.

Yuh (60) used electrochemical impedance spectroscopy and current interruption techniques to characterize the oxygen reduction process on porous NiO in the molten carbonate fuel cell. Yuh determined the activation energy of oxygen reduction to be about 230 kJ/mol and kinetic reaction orders for oxygen and carbon dioxide to be

0.85 and -0.45 , respectively. Lu (23) investigated the oxygen reduction reaction in pure Li_2CO_3 and a Li-K (62 mol%:38 mol%) carbonate eutectic mixture using the potential step method. The exchange current density, determined by Lu (39 mA/cm^2 for 90% O_2 and 10% CO_2 at 750°C in Li_2CO_3 melt), is two orders of magnitude higher than that observed by Appleby and Nicholson (0.34 mA/cm^2), who used the potential-scan technique. The dependence of oxygen reduction kinetics on partial pressures of oxygen and carbon dioxide observed, by Lu, is as follows:

Li_2CO_3 Melt :

$$i_0 = i_0^0 (P_{\text{O}_2})^{0.15 \pm 0.04} (P_{\text{CO}_2})^{-0.10 \pm 0.03} \quad [38]$$

$(\text{Li}, \text{K})_2\text{CO}_3$ Melt :

$$i_0 = i_0^0 (P_{\text{O}_2})^{0.12 \pm 0.03} (P_{\text{CO}_2})^{-0.12 \pm 0.03} \quad [39]$$

The reaction observed by Lu cannot be explained by any of the mechanism proposed in the literature. Uchida *et al.* (61) determined the kinetic parameters for oxygen reduction in a $(\text{Li-K})\text{CO}_3$ (42.7 mol%:57.3 mol%) eutectic melt on a gold electrode using impedance analysis, potential step and coulostatic relaxation methods. They found that the exchange current density was about the same order of magnitude as that observed by Lu. In addition, they concluded that impedance analysis is the most reliable of the three methods for the determination of the kinetic parameters for oxygen reduction in molten carbonates. Uchida *et al.* (62) examined the oxygen reduction on a lithiated NiO film, deposited on gold, and Sb-doped SnO_2 electrodes in Li-K eutectic melt by impedance spectroscopy and coulostatic relaxation techniques. They (63) also determined the temperature dependence of oxygen reduction kinetics on gold in $(\text{Li-K})\text{CO}_3$ and determined the activation energies for the kinetic and mass transfer related parameters. Also, Adanuvor *et al.* (64) showed that a computer simulation is a better approach than the conventional approaches since it can take account of the simultaneous presence of peroxide and superoxide ions with slow neutralization reaction. The simulation results indicate that the melts with high Li-content favor the oxygen reduction kinetics. Ramaswami (65) used a rotating disk

electrode, made of pure gold, to study the oxygen reduction reaction in a pure lithium carbonate melt at 800°C, and determined the diffusion coefficient and peroxide ion concentration as a function of partial pressure of oxygen while keeping the partial pressure of carbon dioxide constant at 0.01 atm.

Nishina and Uchida (66) investigated the oxygen reduction mechanism in molten carbonate electrolytes by electrochemical impedance spectroscopy. They used Randles-Ershler equivalent circuit for a planar gold electrode and the thin film model with the Nernst impedance for a sintered gold electrode to determine Warburg impedance and concluded that the simultaneous diffusion of superoxide ions and carbon dioxide is the dominant path for the oxygen reduction in molten alkali carbonate electrolytes. Makkus *et al.* (67) included the Gericher impedance (i.e., impedance due to the homogeneous chemical reaction) to resolve the impedance spectra for oxygen reduction in (Li-K)CO₃ eutectic melt, but estimated reaction orders for oxygen and carbon dioxide do not agree with the reaction mechanisms proposed in the literature. Makkus *et al.* suggested that diffusing species could be percarbonate ions. Recently, Tryk and Yeager (68) have shown the existence of peroxide and superoxide species in quenched molten alkali carbonates by electron spin resonance spectroscopy and Raman spectroscopy, but the existence of percarbonate ions in the molten carbonate electrolytes has not been published.

Conclusions

The mechanism of oxygen reduction in molten carbonate is not well understood and the results reported in the literature are not consistent. Moreover, oxygen reduction in molten carbonate has fast kinetics, and even near-equilibrium tests reported in the literature indicate mixed-control kinetics. The previous studies show that the presence of physically dissolved molecular oxygen in molten carbonate electrolyte is insignificant. Oxygen reacts with the molten alkali carbonates to form peroxide and/or superoxide ions; the concentrations of these species depend on the cations present in the melt. Thermodynamic data (22) indicate that equilibrium concentration of the superoxide ion decreases with decrease in the ionic radii of the

alkali cations (i.e., $C_{O_2^-}$ decreases in the order $K_2CO_3 > Na_2CO_3 > Li_2CO_3$), and in a pure lithium carbonate melt the superoxide ion is unstable. Consequently, in the present work, pure lithium carbonate melt is used to avoid the complexity of simultaneous formation of peroxide and superoxide ions.

CHAPTER III

OXYGEN REDUCTION IN LITHIUM CARBONATE MELT

Introduction

Study of oxygen reduction in a molten alkali carbonate electrolyte is essential because the overpotential losses in molten carbonate fuel cells are considerably higher at the oxygen cathode compared to those occurring at the fuel anode. The oxygen reduction reaction in molten alkali carbonate electrolyte is very complex because it depends on the cations present in the melt. The previous research efforts (22, 46, 57) have shown that the physical solubility of molecular oxygen in the molten carbonates is very small and oxygen reacts with carbonate ions, present in the melt, to form peroxide and/or superoxide ions, depending upon the cations present in the melt. The peroxide species is dominant in a Li-rich melt, whereas the superoxide species is dominant in a K-rich melt. Both the peroxide and the superoxide ions may be present in the eutectic mixture of 62 mol% Li_2CO_3 and 38 mol% K_2CO_3 (eutectic temperature = 488°C), which is used as an electrolyte in the molten carbonate fuel cell. When the peroxide and the superoxide ions are present simultaneously in the electrolyte, the oxygen reduction mechanism may be a combination of the reaction mechanisms proposed earlier. The formation of the superoxide species is favored by the increase in the cationic radius (or acidity) of the melt, i.e. $\text{C}_{\text{O}_2^-}$ decreases in the order $\text{K}_2\text{CO}_3 > \text{Na}_2\text{CO}_3 > \text{Li}_2\text{CO}_3$. The superoxide species is considered to be unstable in a pure lithium carbonate melt (22). In the present work, a pure lithium carbonate melt is used as an electrolyte to avoid the complexity of simultaneous presence of the peroxide and the superoxide ions in the melt. Also, the lithium carbonate has the lowest melting point ($\sim 723^\circ\text{C}$) among the pure alkali carbonates (69).

In the molten carbonate fuel cell, a porous electrode made of lithiated NiO is used as a cathode. In order to obtain meaningful electrode kinetic parameters, the

electrochemical measurements need to be carried out on a smooth NiO electrode. But, the fabrication of a dense NiO electrode with a well-defined surface area has posed a formidable challenge. Also, the molten alkali carbonate electrolytes are extremely corrosive and most of the metals including noble metals such as platinum and palladium are unstable (28, 36) in these electrolytes and form complex oxides (37). The oxygen reduction reaction has generally been studied on a smooth gold electrode, after Janz and Saegusa (30) showed that gold is "more noble" than platinum in the molten carbonate electrolyte. Since the main objectives of the present work are to elucidate oxygen reduction reaction and to determine the mass transfer and electrode kinetic parameters, a planar gold foil was used as the working electrode. Also, the catalytic effects of the cathode material in the molten carbonate fuel cell may not be very significant because oxygen reduction kinetics is already activated by the high temperature ($\sim 650^\circ\text{C}$). Further, Uchida *et al.* (62) recently showed that the exchange current densities for oxygen reduction in $(\text{Li-K})\text{CO}_3$ have the same order of magnitude on a smooth gold and NiO-coated gold electrodes.

Oxygen Reduction Kinetics in Lithium Carbonate Melt

The oxygen reduction reaction in a lithium carbonate melt was first studied by Silakov *et al.* (70) using the platinum and palladium electrodes. Lorenz and Janz (71) used a gold wire as the test electrode and found that the oxygen reduction mechanism is not the same as that occur at the platinum and palladium electrodes. This discrepancy can be attributed to corrosion of the platinum and palladium metals in molten alkali carbonates (36, 28). They attributed the cathodic current at low overpotentials to the reduction of both oxygen and carbon dioxide to form carbonate ions (Eqn. [40]), which was proposed by Stepanov and Trunov (35):

The direct oxygen reduction reaction (Eqn. [41]) was proposed for the cathodic current at overpotentials more negative than -0.3 V :

Appleby and Nicholson (46) investigated the oxygen reduction reaction on a submerged gold electrode using steady-state and potential sweep techniques. They specified the difference in electrochemical behavior of the meniscus electrode (e.g., an electrode with three-phase boundary) used by previous investigators and fully-immersed electrode. They showed that the diffusion-controlled peak depends on the partial pressures of oxygen (P_{O_2}) and carbon dioxide (P_{CO_2}). Based on this observation, they proposed that molecular oxygen reacts with the carbonate ions in the melt to form peroxide ions and carbon dioxide; the peroxide ions are reduced in two electron transfer steps to form oxide ions which recombine with carbon dioxide to form carbonate ions. The reaction mechanism for oxygen reduction in a lithium carbonate melt, proposed by Appleby and Nicholson, is as follow:

Overall Reaction

According to this mechanism, the first electron transfer step (Eqn. [43]) is rate determining for a submerged gold electrode and (O^-) is a transient species. The recombination reaction (Eqn. [45]) may be slow and the accumulation of oxide ions at the electrode surface will increase the effective melt basicity of melt in the vicinity of the electrode. In the porous electrode of a molten carbonate fuel cell, the recombination reaction could be the rate determining step. Appleby and Nicholson observed a shift in the peak potential with scan rate and high values of capacitance currents at high scan rates. The latter phenomenon indicates the formation of a solid oxide layer on the gold electrode surface.

Lu (23) examined the oxygen electrode on a fully-immersed gold electrode in a lithium carbonate melt at 750°C using potential step and potential sweep

techniques. He determined the electrode kinetic parameters, exchange current density and apparent transfer coefficient, as functions of partial pressures of oxygen and carbon dioxide. The exchange current density (38.7 mA/cm^2 for oxidant gas of 0.9 atm PO_2 and 0.1 atm PCO_2 at 750°C) was determined in this work from the potential step data and was found to be about two order of magnitude higher than that (0.34 mA/cm^2) obtained by Appleby and Nicholson (46), who used the potential sweep technique. Lu concluded that the exchange current density determined from the potential sweep data is inherently underestimated. He also showed that the neutralization reaction (Eqn. [45]) is slow. The rate constant of the recombination reaction was shown to increase with temperature and the activation energy of this reaction was determined to be about 19.1 kJ mol^{-1} . Lu also showed that the oxide ions produced by oxygen reduction, during the steady state measurements and potential sweep, may accumulate at the electrode-electrolyte interface causing an increase in the effective basicity of the melt at the interface; this increase in the basicity at the interface shifts the electrode potential in the negative direction. Lu determined the reaction orders of the exchange current density to be about $+0.15$ for partial pressure of oxygen and -0.10 for carbon dioxide; these values of the reaction orders cannot be explained by any of the reaction mechanisms proposed in the literature.

Adanuvor *et al.* (64) simulated the oxygen reduction reaction on a rotating disk electrode for different cations present in the melt and concluded that melts with high Li-content should yield the highest electrode kinetic rates. Ramaswami (65) investigated the oxygen reduction in lithium carbonate melt using a rotating disk electrode made of gold and linear sweep voltammetry. He determined the diffusion coefficient and the concentration of the peroxide ions as a function of partial pressure of oxygen, at 800°C and 0.01 atm partial pressure of carbon dioxide, from the limiting currents and the results of potential step measurements. The diffusion coefficient of the peroxide ions was estimated to be about $3.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and the value of the diffusion coefficient was found to be independent of the concentration of the peroxide ions. Ramaswami also determined the rate constant of the recombination reaction (Eqn. [45]) by the analysis of the potential response to oxide addition.

The recombination rate constant for lithium carbonate melt at 800°C is about $4.1 \times 10^{-3} \text{ s}^{-1}$.

These studies show that (i) the reaction mechanism for oxygen reduction in molten alkali carbonates is not well understood, even for the simplest melt like lithium carbonate where only the peroxide species is present, and (ii) the experimental data could not be explained by the mechanisms available in the literature. In the present work the oxygen electrode reaction in lithium carbonate melt on a fully-immersed gold electrode is examined by electrochemical impedance spectroscopy and cyclic voltammetry.

Experimental Setup

The experimental setup to investigate the electrode kinetics of oxygen reduction in molten alkali carbonate electrolytes is shown, schematically, in Fig. 2. The experimental setup is similar to that used by other researchers (43, 46, 23) to study oxygen reduction kinetics in molten carbonate electrolyte. The experimental setup consists of the following: (i) high temperature furnace system; (ii) electrochemical cell assembly; (iii) gas flow measurement/purification system; and (iv) electrochemical measurement system.

High Temperature Furnace System

This system consisted of (a) a three-zone, split-type, tubular furnace with an individual thermocouple for each zone, (b) a temperature control system with three microprocessor-based controllers and display devices, (c) outer alumina tube for the controlled environment around the electrochemical cell, and (d) the stainless steel header.

A three zone (each zone 6" long) split-tube furnace (Model 3210) rated for a maximum temperature of 1200°C. was used to heat the electrochemical cell. Each heating zone was provided with a thermocouple (Type K Chromel/Alumel) and a microprocessor-based controller for separate control to obtain uniform temperature distribution in the electrochemical cell. The electrochemical cell was kept in the

Fig. 2. Experimental Setup for Electrode Kinetic Studies.

central zone of the furnace. The stainless steel header, shown in Fig. 2, served several purposes. Firstly, the electrochemical cell was suspended from its bottom into the outer alumina tube which was used as an outer jacket in the tube furnace. Secondly, the electrodes, thermocouple, and gas inlet-outlet tubes were fitted by "O" rings through the header. Lastly the header served as a cooling device to protect the fittings. The electrochemical cell was suspended from a stainless steel header using alumina tubings and an alumina bottom plate connected by the gold wires. Several pierced alumina baffles with spacers were used to decrease the convective heat transfer in order to minimize the temperature gradient within the cell. The cell temperature was monitored by Type K Chromel-Alumel thermocouple (Omega) enclosed in a closed end alumina tube, which was firmly pressed against the bottom of the cell. The electrochemical cell and the hanging assembly were enclosed by an outer alumina jacket. The alumina jacket (outer diameter 6.25 cm and length 76 cm, McDanel Refractory Co.) was held by the header using an "O" ring so that the electrochemical cell assembly was hermetically sealed. The "O" rings used were made of Viton material (National O-rings/Technical Sales Inc.) which could withstand high temperature. The stainless steel header also had a cooling coil to protect the "O" rings.

Electrochemical Cell Assembly

The electrochemical cell was made of a recrystallized alumina cylinder of 99.8% purity, obtained from McDanel Refractory Co., with a capacity of about 90 cm³. The working electrode was made of a submerged gold flag (0.0025 cm thick) and geometrical area of about one square centimeter (0.7 cm × 0.7 cm). It was connected to a gold current collector (0.05 cm diameter) by a thin gold wire to minimize the meniscus effect (46, 72) because the presence of a meniscus modifies the electrochemical response considerably (65, 73). The counter electrode consisted of a large gold foil which was used as an inner liner of the cell to ensure uniform current distribution. The current collectors of the working and the counter electrodes were encased by alumina tubings (diameter 0.635 cm) and the tubings were sealed outside the stainless steel header by

Swagelock fittings. The reference electrode was also made of a gold foil, but encased in an alumina tube (diameter 0.635 cm) which was pressed against the bottom of the electrochemical cell. The Puratronic grade (99.99%) gold foils and wires were obtained from Johnson Matthey/ÆSAR Group.

Gas Flow Measurement/Purification System

Individual mass flow controllers/meters (HFC-202, Teledyne-Hastings Raydist) were used for O₂, CO₂ and Ar gases to provide the gas mixtures of the desired compositions with high accuracy ($\pm 1\%$ Full Scale). The mass flow controllers were powered by a 4-channel power supply (PR-4A) which was also used for read out. The high purity gases were obtained from Matheson Gas Products and traces of water were removed by passing the blended gas through a column of 5 Å molecular sieves and Drierite (Fisher Scientific). The gas mixture was bubbled into the melt in the vicinity of the working electrode at a flow rate of about 50 cm³ min⁻¹ through a long alumina tube with four pinholes to form smaller bubbles for enhanced mass transfer. The composition of the gas mixture supplied to the reference electrode compartment was the same as the one used for the working electrode, but at a flow rate of about 5 cm³ min⁻¹.

Electrochemical Measurement System

The data acquisition setup consisted of a potentiostat/galvanostat (PAR Model 273), lock-in-amplifier (PAR Model 5301A), personal computer (IBM PS/2), and software (PAR Headstart and Model 378) obtained from EG&G Princeton Applied Research. This setup was used for cyclic voltammetry and electrochemical impedance measurements.

Prior to the experiment, all metallic and ceramic components were rinsed with high purity water and cleaned with acetic acid and hydrochloric acid. The final washing was carried out by high purity water and ultrasonication. The ultra-high purity (18 MΩ cm resistivity) water, used for the pretreatment of the cell components, was obtained by Nanopure water purification system. The electrodes, gas sparger,

and thermocouple in an alumina tube were assembled and fitted through the header by using "O" rings made of Viton. The electrochemical cell was suspended from the header. The entire assembly was dried at 200°C for 24 hours. The high purity (99.999%) lithium carbonate (Alfa Products) was carefully weighed and transferred to the electrochemical cell. The outer alumina jacket was then fitted into the header by using a Viton "O" ring and the entire electrochemical cell assembly was hermetically sealed. The electrochemical cell assembly was slowly heated (50°C/hr) to 350°C under an inert (e.g., argon) environment. The electrochemical cell assembly was kept at 350°C in a carbon dioxide environment for 24 hours before heating to 750°C. The electrochemical cell was kept in the carbon dioxide environment for 24 hours at 750°C. The molten lithium carbonate was equilibrated with the gas mixture of desired composition for at least 12 hours prior to the electrochemical measurements. The potential difference between the working and the counter electrode was constantly monitored by a multimeter.

Cyclic Voltammetry

Cyclic voltammetry measurements were made in a quiescent lithium carbonate melt as a function of scan rate for the gas composition of 90% O₂ and 10% CO₂ at 850°C (Fig. 3). During the potential scan, gas flow through the sparger was stopped, and the gas was blanketed on top of the electrochemical cell. Between two subsequent potential scans, the electrolyte was equilibrated with the gas mixture for several minutes. The potential scans were carried out between the rest potential (~ 0.0 V) of the working electrode and -0.5 V vs. the reference electrode. The scan rates were varied from 10 mV/s to 200 mV/s. During the forward scan, a diffusion-controlled peak, followed by a limiting plateau, was observed. Appleby and Nicholson (46) observed similar behavior in their investigation of oxygen reduction in a pure lithium carbonate melt by potential scan technique. They attributed this behavior to the reduction of peroxide ions. The current densities in the reverse scan were observed to be less cathodic than those in the forward sweep and for overpotential less negative than -0.1 V, positive (anodic) current densities were observed. When the applied

potential returned to the initial potential, a large anodic current was observed. The anodic current density, observed at the end of the sweep, subsided slowly and reached to zero in few minutes; this anodic current density was proportional to the charge passed in the forward sweep. Lu (23) made a similar observation for oxygen reduction on gold in the eutectic mixture of lithium and potassium carbonates. This behavior is due to the local accumulation of oxide ions which shifts the reversible electrode potential in negative direction. Borucka (74) suggested that the electrode potential for $(\text{O}_2, \text{CO}_2/\text{CO}_3^{2-}(\text{Au}))$ depends on the local activity of oxide ion at the electrode-electrolyte interface and that the reversible electrode potential is represented by the Nernst equation:

$$E_{\text{O}_2, \text{CO}_2/\text{CO}_3^{2-}} = E_{\text{O}_2/\text{O}^{2-}}^{\circ} + \frac{RT}{2F} \ln \left(\frac{P_{\text{O}_2}^{1/2}}{a_{\text{O}^{2-}}} \right) \quad [47]$$

where,

$$E_{\text{O}_2/\text{O}^{2-}}^{\circ} = E_{\text{O}_2, \text{CO}_2/\text{CO}_3^{2-}}^{\circ} + \frac{RT}{2F} \ln K_d \quad [48]$$

Lu (23) and Ramaswami (65) showed that addition of solid Li_2O pellet to the molten alkali carbonate electrolyte shifts the potential of the submerged gold electrode in a negative direction, which returns to the original value in a few minutes. The magnitude of the potential shift and time taken to return to the original value depends on the amount of oxide added, gas composition and cations present in the melt.

As shown in Fig. 3, the peak potential value did not vary with the scan rate. The peak potential was about 40-45 mV negative to the equilibrium potential, which corresponded to $RT/2F$, indicating that two electrons were involved during oxygen reduction reaction. Other researchers (23, 61, 65) have made similar observation for oxygen reduction in molten alkali carbonates. Appleby and Nicholson (46) observed a negative shift in the peak potential for O_2 reduction in pure Li_2CO_3 which may have been due to the uncompensated electrolyte resistance. The uncompensated electrolyte resistance causes the peak potential (E_p) to be a function of the scan rate and shifts the peak potential in a negative direction with an increase in the scan rate, even for a reversible electrode reaction (75). Appleby and Nicholson (46)

Fig. 3. Effect of Scan rate on the Cyclic Voltammogram for O_2 Reduction on a Submerged Gold Electrode in Lithium Carbonate Melt at 850°C.

suggested that the diffusion-controlled wave for oxygen reduction in Li_2CO_3 melt can be described by the case of constant product activity because the final product is the carbonate ions. Berzins and Delahay (76) have solved the boundary value problem of continuously changing potential applied to the electrochemical system with the following conditions: (i) electrochemically reversible (very fast) reaction; (ii) linear diffusion; and (iii) the product activity is invariant and equal to unity (e.g., metal deposition). They derived the following expression for the current response as a function of potential sweep.

$$i = \frac{2}{\pi^{1/2}} \frac{(nF)^{3/2}}{(RT)^{1/2}} C_O D_O^{1/2} v^{1/2} \Phi \left[\left(\frac{nF}{RT} t \right)^{1/2} \right] \quad [49]$$

where, i is the current density, n is the number of electrons involved in the electrochemical reaction, v is the scan rate, and D_O and C_O are the diffusion coefficient and the bulk concentration of the diffusing species, respectively. The function $\Phi[\lambda]$ is represented by the following expression (77):

$$\Phi[\lambda] = \exp(-\lambda^2) \int_0^\lambda \exp(z^2) dz \quad [50]$$

where z is an auxiliary variable. The function Φ has a maximum value of 0.541 when the argument λ is 0.924 (78) and the peak current density is

$$i_p = 0.61 \frac{(nF)^{3/2}}{(RT)^{1/2}} C_O D_O^{1/2} v^{1/2} \quad [51]$$

According to Eqn. [51], the peak current density (i_p) should vary linearly with the square root of the scan rate ($v^{1/2}$). The slope of this plot is proportional to $D_O^{1/2} C_O$ and knowledge of one of these quantities will yield the other. The linear behavior of i_p vs. $v^{1/2}$ and invariance of the peak potential with the scan rate indicated that the oxygen reduction on a submerged gold electrode in a pure lithium carbonate is "reversible" up to 200 mV/s (79).

Electrochemical Impedance Spectroscopy

Electrochemical impedance analysis is a powerful spectroscopic technique based on the same principle that is fundamental to process control. When a linear system

is perturbed by an excitation function (e.g., sinusoidal voltage signal), the response (current) is related to the input signal by a transfer function (impedance). The transfer function, also known as an impulse response function, describes the dynamic characteristics of the linear system. The system is perturbed by imposing a small amplitude, sinusoidal voltage signal of frequency ω . The system responds to this alternating voltage signal by relaxing to a new pseudo-steady state. The resultant current signal will have the same frequency ω , but an amplitude different from the input signal which is phase shifted, provided that higher harmonic response is negligible. The transfer function (impedance) which relates response to the input, is defined as a ratio of the alternating voltage to the alternating current. The electrochemical impedance spectroscopy (EIS) has the following advantages over steady-state and time-domain transient techniques (80 - 82): (i) since the amplitude of the sinusoidal, perturbation signal is small, the electrochemical interface is virtually undisturbed, which is not the case when the steady state techniques are used and the electrode electrolyte interface changes due to a very large magnitude of the input signal; (ii) the small amplitude of the perturbation signal makes it possible to treat the output signal by a linear-response analysis. This analysis leads to important simplifications in treating kinetics and diffusion, and (iii) its ability to separate physico-chemical phenomena such as double layer charging, charge-transfer kinetics, and mass transfer process, which is the biggest advantage of the EIS technique.

The electrochemical system is perturbed by superimposing a small amplitude voltage signal, $\tilde{V} = |\tilde{V}| \sin(\omega t)$, of frequency ω ; the system then responds to this sinusoidal voltage by relaxing to a new pseudo-steady state. The resultant alternating current output, $\tilde{i} = |\tilde{i}| \sin(\omega t - \phi)$, will have the same frequency ω , but different amplitude and will be phase shifted from the input signal. The total impedance Z of the electrochemical system is the ratio of the alternating voltage to the current response and is described by the following equations:

$$\begin{aligned} Z &= \frac{\tilde{V}}{\tilde{i}} \\ &= |Z| \exp(j\phi) \\ &= Z' - jZ'' \end{aligned} \quad [52]$$

The magnitude of the total impedance

$$\begin{aligned} |Z| &= \frac{|\tilde{V}|}{|\tilde{i}|} \\ &= \sqrt{(Z')^2 + (Z'')^2} \end{aligned} \quad [53]$$

is expressed in $\Omega\text{-cm}^2$, and the phase shift between the current and the potential is given by

$$\phi = \arctan \left(\frac{Z''}{Z'} \right). \quad [54]$$

The impedance analysis was carried out by using the equivalent circuit model shown in Fig. 4. This model is referred to as the Randles-Ershler equivalent circuit model (83, 84) and consists of two parallel paths for the two parallel processes occurring at the electrode-electrolyte interface. These processes are double layer charging and faradaic charge transfer. The faradaic impedance consists of the charge transfer resistance and the diffusional impedance in series. The uncompensated resistance between the reference and the working electrodes is given by R_s which is in series with the rest of the circuit.

Impedance analysis by the Randles-Ershler equivalent circuit model is based on the following assumptions (80, 82): (i) linearized current-potential characteristic is applicable because the amplitude of the sinusoidal perturbation signal is small and impedance measurements were made at the equilibrium potential of the working electrode; (ii) semi-infinite boundary condition for the mass transfer (i.e., in the region far away from the electrode, the bulk concentrations of the species are unperturbed); (iii) uniform current distribution on a planar working electrode (i.e., the working electrode is large enough so that deviations from homogeneity of the electric field at the edges is negligible and the counter electrode completely surrounds the working electrode); (iv) *a priori* separation of the faradaic process and the double layer structure (i.e., the faradaic impedance and the double layer reactance are independent of each other); (v) only the fundamental harmonic response is considered (i.e., the amplitude of the perturbation signal is small enough, so that the higher harmonic response, due to the dependence of the double layer capacitance on a voltage across

- R_s = Solution Resistance, $\Omega \text{ cm}^2$
 R_{ct} = Charge Transfer Resistance, $\Omega \text{ cm}^2$
 C_{dl} = Double Layer Capacitance, Farad cm^{-2}
 Z_W = Warburg Impedance, $\Omega \text{ cm}^2$

Fig. 4. Randles-Ershler Equivalent Circuit.

the interface and the exponential dependence of the faradaic current on the surface overpotential, is negligible); (vi) mass transfer is due to diffusion only (i.e., negligible influence of migration and convection); (vii) frequency dispersion of the double layer capacitance is negligible and (viii) charge transfer takes place at the interface where there is no specific adsorption.

The expressions for the real (Z') and the imaginary (Z'') part of the total impedance (Z) are as follow (82):

$$\begin{aligned} Z &= R_s + \frac{1}{[(R_{ct} + Z_W)^{-1} + j\omega C_{dl}]} \\ &= Z' - jZ'' \end{aligned} \quad [55]$$

where,

$$Z' = R_s + \frac{R_{ct} + \sigma/\sqrt{\omega}}{(C_{dl}\sigma\sqrt{\omega} + 1)^2 + \omega^2 C_{dl}^2 (R_{ct} + \sigma/\sqrt{\omega})^2} \quad [56]$$

$$Z'' = \frac{\omega C_{dl}(R_{ct} + \sigma/\sqrt{\omega})^2 + \sigma/\sqrt{\omega}(C_{dl}\sigma\sqrt{\omega} + 1)}{(C_{dl}\sigma\sqrt{\omega} + 1)^2 + \omega^2 C_{dl}^2 (R_{ct} + \sigma/\sqrt{\omega})^2} \quad [57]$$

The complex plane impedance plot for a quasi-reversible reaction is shown schematically in Fig. 5. The impedance spectrum distinguishes various phenomena because of the variation in the relaxation times of these processes. The complex plane plot yields information on phenomena such as double layer charging, charge-transfer reactions, ohmic resistance, and mass transfer process in the electrolyte. Two regions of interest are defined by the conditions: $\omega \rightarrow 0$ and $\omega \rightarrow \infty$.

As $\omega \rightarrow 0$, the Eqns. [56] and [57] approach the following limiting forms:

$$Z' = R_s + R_{ct} + \sigma/\sqrt{\omega} \quad [58]$$

$$Z'' = \sigma/\sqrt{\omega} + 2\sigma^2 C_{dl} \quad [59]$$

which upon elimination of ω yields

$$Z'' = Z' - R_s - R_{ct} + 2\sigma^2 C_{dl} \quad [60]$$

Hence at low frequencies the complex plane plot yields a straight line of 45° slope whose high-frequency intercept on the real axis is $R_s + R_{ct} - 2\sigma^2 C_{dl}$.

Fig. 5. The Complex Plane Impedance Plot for a Quasi-reversible Electrochemical Reaction.

In the second case $\omega \rightarrow \infty$ and the real and imaginary components of the total impedance attain their limiting values,

$$Z' = R_s + \frac{R_{ct}}{(1 + \omega^2 C_{dl} R_{ct}^2)} \quad [61]$$

$$Z'' = \frac{\omega C_{dl} R_{ct}^2}{(1 + \omega^2 C_{dl} R_{ct}^2)} \quad [62]$$

Again, elimination of frequency yields a following expression:

$$\left(Z' - R_s - \frac{R_{ct}}{2} \right)^2 + (Z'')^2 = \left(\frac{R_{ct}}{4} \right)^2 \quad [63]$$

Hence a plot of Z' vs. Z'' gives a semicircle centered at $Z' = R_s + R_{ct}/2$ and $Z''=0$ and having a radius of $R_{ct}/2$.

Since oxygen reduction in molten carbonate is very facile, the charge transfer resistance is much smaller compare to the Warburg impedance and the ohmic resistance and the semicircular region is not well defined. Impedance analysis based on the Randles-Ershler equivalent circuit model estimates four parameters, namely, the charge transfer resistance (R_{ct}), double layer capacity (C_{dl}), Warburg coefficient (σ), and solution resistance (R_s).

Impedance Measurements and Analyses

The wide range of frequency, from 0.05 Hz to 10 kHz, was used for the small signal perturbation because the capacitive effect attributed to the double layer is significant at high frequency whereas the mass transfer related (Warburg) impedance is dominant at low frequency.

The impedance measurements for frequencies higher than 5 Hz were carried out using the Phase Sensitive Detection (PSD) technique with a lock-in-amplifier and a potentiostat. In the Phase Sensitive Detection technique, the impedances are measured in the frequency domain: the voltage excitation signal is applied simultaneously to the electrochemical cell and a reference channel. The cell response (current signal) is compared with the perturbing signal, using a phase sensitive

detector. Usually it is not possible to measure a cell impedance by the PSD technique when the excitation signal frequency is below 1 Hz. Hence, for the perturbation signal of frequency below 5 Hz, the cell impedance was measured by the Fast Fourier Transform (FFT) technique using a personal computer and a potentiostat.

The FFT is a time domain technique in which a digitally generated pseudo-random white noise signal (i.e., the algebraic sum of many individual wave forms of equal amplitude but having a different frequency and phase characteristics) is used as a perturbing signal and the complex response to this signal is resolved by an inverse Fast Fourier Transform into discrete frequency data. The FFT technique has a major advantage over frequency domain methods for low frequency measurement because the data can be obtained considerably faster. The low frequency measurements (below 5 Hz) reported here are average of 15 data cycles to improve the accuracy of the data by averaging out the noise interference.

The amplitude of a perturbation signal needs to be small to ensure linear response of the electrochemical system i.e., to decrease the influence of higher harmonics on the measured impedance. The lower limit for the amplitude is determined by the signal-to-noise ratio which can be accepted by the measuring instrument, whereas the high limit is determined by the onset of nonlinear distortion (85, 86). We investigated the impedance spectra for oxygen reduction, on gold in lithium carbonate melt at 750°C, as a function of the excitation signal amplitude and observed that the effect of amplitude on the impedance spectra was insignificant when the amplitude of the perturbation signal was varied from 3 to 9 mV, indicating that measurements were in the linear domain. Hence, all the measurements reported here were obtained using an excitation signal amplitude of 5 mV. The impedance measurements were carried out at the equilibrium potential over the frequency range of 0.05 Hz to 10 kHz. The complex plane plot for the impedances measured at 750°C and 90% O₂ and 10% CO₂ gas composition is shown in Fig. 6. The absence of a semicircle in the complex plane plot indicated fast electrode kinetics (87). In the region of low frequency, the complex plane impedance plot shows a linear behavior with a slope of 45° due to the mass transfer related (Warburg) impedance (88). The complex plane plot for frequencies

higher than 100 Hz is shown in the inset in Fig. 6. In the region of high frequency, the imaginary part of the impedance (Z'') diminished with increasing frequency and approached zero at about 10 kHz.

Impedance Analysis Using Complex Plane Plots

The uncompensated solution resistance was determined to be 0.38Ω for the impedance spectrum shown in Fig. 6 by the high frequency limits of Eqns. [56] and [57]:

As $\omega \rightarrow \infty$,

$$Z' = R_s \quad [64]$$

$$Z'' = 0 \quad [65]$$

The charge transfer resistance, Warburg coefficient, and double layer capacity were determined by the frequency variation of impedance and admittance spectra in a low frequency region.

As $\omega \rightarrow 0$, the Eqns. [56] and [57] approach the following limiting forms:

$$Z' = R_s + R_{ct} + \sigma/\sqrt{\omega} \quad [66]$$

$$Z'' = \sigma/\sqrt{\omega} + 2\sigma^2 C_{dl} \quad [67]$$

Using Eqn. [66], the Warburg coefficient (σ) was calculated to be $80.7 \Omega s^{1/2}$ from the slope of a Z' vs. $\omega^{-1/2}$ plot in the low frequency region (0.15 Hz to 30 Hz), which is shown in Fig. 7. By substituting Eqn. [67] into Eqn. [66], we get:

$$Z'' = Z' - R_s - R_{ct} + \sigma^2 C_{dl} \quad [68]$$

The complex plane plot for impedance data in a low frequency region is shown in Fig. 8: slope of this plot is equal to unity and the intercept is expressed by:

$$\text{intercept} = -R_s - R_{ct} + \sigma^2 C_{dl} \quad [69]$$

Fig. 6. Complex Plane Plot for Impedance Spectrum Measured at the Rest Potential; The Inset Figure is a Magnified Plot for the High Frequency Data.

Fig. 7. Plot of Z' vs. $\omega^{-1/2}$ for Estimation of Warburg Coefficient.

Since the uncompensated solution resistance was already determined from the high frequency limits, the interfacial admittance (Y_{el}) can be expressed by the following expressions:

$$Y_{el} = Y'_{el} + jY''_{el} \quad [70]$$

$$Y'_{el} = \frac{Z' - R_s}{(Z' - R_s)^2 + (Z'')^2} \quad [71]$$

$$Y''_{el} = \frac{Z''}{(Z' - R_s)^2 + (Z'')^2} \quad [72]$$

By substituting Eqns. [56] and [57] into Eqns. [71] and [72] and using a parameter $p = R_{ct}/\sigma\omega^{-1/2}$:

$$Y'_{el} = \frac{\omega^{1/2}}{\sigma} \frac{p+1}{p^2+2p+2} \quad [73]$$

$$Y''_{el} = \frac{\omega^{1/2}}{\sigma} \frac{1}{p^2+2p+2} + \omega C_{dl} \quad [74]$$

By substituting Eqn. [73] into Eqn. [74]:

$$Y''_{el} = \frac{Y'_{el}}{p+1} + \omega C_{dl} \quad [75]$$

The parameter p plays an important role in the separation of charge transfer resistance from the Warburg coefficient because it indicates the mode of control over the faradaic impedance: charge transfer resistance is dominant when $p \rightarrow \infty$ and mass transfer (Warburg) impedance is controlling when $p \rightarrow 0$ (80). Hence p is much less than 1 in the low frequency region where the mass transfer related impedance is dominant, and Eqn. [75] can be approximated by the following expression:

$$\frac{Y''_{el}}{\omega} = \frac{Y'_{el}}{\omega} + C_{dl} \quad [76]$$

As shown in Fig. 9, plot of Y''_{el}/ω vs. Y'_{el}/ω showed a linear behavior with a slope of 45° and double layer capacitance was determined to be $301.4 \mu F \text{ cm}^{-2}$ from the intercept. The charge transfer resistance was calculated to be 1.03Ω , by substituting the values of σ , R_s and C_{dl} into Eqn. [13]. The parameters estimated by this technique are given in Table 3.

Fig. 8. Complex Plane Impedance Plot in a Region of Low Frequency to Determine Charge Transfer Resistance.

Fig. 9. Plot of Y_{el}''/ω vs. Y_{el}'/ω to Determine Double Layer Capacitance.

Table 3. Comparison of Kinetic and Mass Transfer Parameters Estimated by Complex Plane Plots and Complex Nonlinear Least Square Technique; Temperature: 750°C; Gas Composition: 90% O₂ and 10% CO₂.

Method	σ $\Omega \text{ cm}^2 \text{ s}^{-1/2}$	R_{ct} $\Omega \text{ cm}^2$	C_{dl} $\mu\text{F cm}^{-2}$	R_s $\Omega \text{ cm}^2$
Complex Plane Plots	82.5	0.95	276	0.38
CNLS	81.3±2.5	0.95±0.48	301±17	0.38

Impedance Data Analysis by Nonlinear Parameter Estimation

A Complex Nonlinear Least Square (CNLS) parameter estimation program (89, 91) was used with the Randles-Ershler equivalent circuit model (Eqns. [56] and [57]) to analyze impedance spectrum and determine kinetic and mass transfer related parameters. The CNLS program is based on the modified Levenberg-Marquardt algorithm (92, 93). The objective function, $f(\mathbf{X})$ which is to be minimized, is the sum of squares of the weighted-residual error between the experimentally observed data and the values predicted by the equivalent circuit model. Mathematically, $f(\mathbf{X})$ is expressed as:

$$f(\mathbf{X}) = \sum_{i=1}^N [w'_i(Z'_{\text{exp},i} - Z'_{\text{mod},i})^2 + w''_i(Z''_{\text{exp},i} - Z''_{\text{mod},i})^2] \quad [77]$$

where, $\mathbf{X}$ is the vector of the unknown parameters to be evaluated, Z'_i and Z''_i are the real and the imaginary parts of the impedance, and w'_i and w''_i are the weighting factors for the real and the imaginary parts of the impedance, respectively. In this analysis, it was found that the weighting factor (inverse of the error variance) considerably influenced the accuracy of the parameters estimated from the impedance data. In the CNLS program, the impedance data can be weighted in various ways such as unit weighting (UWT), modulus weighting (MWT), and proportional weighting (PWT) (94). The UWT means w'_i and w''_i are equal to one, and all data are weighted evenly. The MWT means w'_i and w''_i are the same and equal to inverse of the modulus ($|Z|$) of the data points. The PWT means the uncertainties associated with the real and the imaginary components of the data are proportional to their magnitudes. The selection of the weighting was carried out by computer generated impedance spectrum using the Randles-Ershler equivalent circuit model and the parameters estimated by the complex plane plots. The "synthetic" data were obtained by adding random errors. The effect of weighting factor on the accuracy of the estimated parameters was determined for the different levels of random errors (1%, 2%, and 5% of the magnitude). The accuracy of the estimated parameters decreased with increase in the magnitude of random error: the error in the estimated

parameters was most pronounced for the UWT and the least for the proportional weighting. Hence, the proportional weighting factor was used to estimate the charge transfer resistance, double layer capacity and Warburg coefficient from the impedance data. As shown in a complex plane plot in Fig. 6, the model impedance data, calculated using the estimated parameters and the Randles-Ershler equivalent circuit model (Eqns. [56] and [57]), were consistent with the experimental data. Since the impedance measurements were obtained at the equilibrium potential, the charge transfer resistance can be expressed as follows (80):

$$R_{ct} = \frac{RT}{nFi_o} \quad [78]$$

By using Eqn. [78], the exchange current density for oxygen reduction reaction on a gold electrode was calculated to be 44.0 mA cm^{-2} . As shown in Table 1, the parameters estimated by the complex plane plot methods and the CNLS technique are in good agreement. The complex plane plot technique utilizes the impedance data in a low frequency region only, whereas the computer curve fitting CNLS method uses the entire impedance spectrum. Hence, the parameters estimated by the CNLS technique can be expected to be more reliable than those obtained by the complex plane plots.

Conclusions

The cyclic voltammogram showed a diffusion-limited peak followed by a limiting current plateau. The peak potential did not vary with the scan rate and the peak potential was $\sim 45 \text{ mV}$ ($RT/2F$) negative of the equilibrium potential, indicating that the oxygen reduction in a pure lithium carbonate melt involves two electrons. The linear variation of the peak current density with the square root of the scan rate and invariance of the peak potential with respect to the scan rate showed the oxygen reduction reaction in a pure lithium carbonate melt is "reversible" up to 200 mV/s . Since the complex plane impedance plot did not show a semicircular relaxation, the electrochemical impedance spectrum indicated that electrode kinetics of oxygen.

reduction reaction in a pure lithium carbonate melt are very rapid. In a region of low frequency, the complex plane impedance plot showed a linear behavior with a slope of 45° indicating that the diffusional process is dominant. The electrochemical impedance spectra were analyzed by the complex plane plots (graphical analysis) and CNLS program based on Levenberg-Marquardt algorithm. The electrode kinetic and mass transfer parameters determined by the graphical and CNLS analyses agreed well. The parameters obtained by the CNLS technique not only have better accuracy, but it also provide the confidence limits for the estimated parameters.

CHAPTER IV

EFFECTS OF TEMPERATURE

Introduction

The oxygen reduction process in molten alkali carbonate electrolyte has been studied for the past 25 years because of its vital role in the performance and stability of the molten carbonate fuel cell. Appleby and Nicholson (45 - 47) examined the oxygen reduction reaction in molten carbonates on a submerged gold electrode using steady state and potential scan techniques. They observed that oxygen reacts with carbonate ions and forms peroxide and superoxide ions and the concentrations of these species depend on the cations present in the melt. In a pure Li_2CO_3 or a Li-rich melt the peroxide species is dominant, whereas in a K-rich melt the superoxide species is dominant. Hence, the oxygen reduction mechanism strongly depends on the cations present in the melt. Andersen (22) carried out a thermodynamic study on the chemical equilibria in molten alkali carbonate electrolytes and demonstrated the presence of peroxide ions by the quenching experiments followed by chemical analyses. Vogel *et al.* (57) studied the (Li-K) CO_3 eutectic melt at 650°C , using a rotating gold wire and concluded that superoxide is dominant in this melt and the amount of molecular oxygen in the melt is negligible. White and Twardoch (59) examined the (Li-Na-K) CO_3 eutectic melt at 680°C by cyclic voltammetry, chronopotentiometry, and chronoamperometry and observed the simultaneous presence of peroxide and oxide ions. Dunks and Stelman (53) studied pure sodium carbonate melt at 900°C and proposed the presence of percarbonate ions. Lu (23) investigated the oxygen reduction reaction in pure Li_2CO_3 and a Li-K (62 mol%:38 mol%) carbonate eutectic mixture using a potential step method. The exchange current density, determined by Lu, is two orders of magnitude higher than that observed by Appleby and Nicholson, who used the potential scan technique. But the dependence of oxygen reduction kinetics on partial pressures of oxygen and carbon dioxide observed by Lu could not

be explained by any of the mechanisms proposed in the literature. Uchida *et al.* (61) determined the kinetic parameters of oxygen reduction in a (Li-K)CO₃ (42.7 mol%:57.3 mol%) eutectic melt on a gold electrode using electrochemical impedance spectroscopy, potential step and coulometric relaxation methods. They found that the exchange current density was about the same order of magnitude as that observed by Lu. In addition, they concluded that the electrochemical impedance spectroscopy is the most reliable of the three methods for the determination of the kinetic parameters for oxygen reduction in molten carbonates. Uchida *et al.* (62) examined the oxygen reduction on a lithiated NiO film, deposited on gold, and Sb-doped SnO₂ electrodes in Li-K eutectic melt by impedance spectroscopy and coulometric relaxation techniques. They (63) also determined the temperature dependence of oxygen reduction kinetics on gold in (Li-K)CO₃ and determined the activation energies for the kinetic and mass transfer processes.

These studies show that (i) oxygen reduction kinetics in molten alkali carbonate strongly depends on the cations present in the melt; (ii) the mechanism for the oxygen reduction in molten carbonate is not well understood; and (iii) the results reported in the literature are contradictory. Consequently, in the present work, we used pure lithium carbonate melt to avoid the complexity of simultaneous presence of peroxide and superoxide ions. The oxygen reduction reaction on a submerged gold electrode was studied using electrochemical impedance spectroscopy (EIS) and cyclic voltammetry to determine the kinetic and transport parameters. Also, the influence of temperature on the oxygen reduction kinetics was examined and the apparent activation energies were calculated.

Experimental

The experimental arrangement and the electrochemical cell assembly used for this work are shown in Fig. 2. The electrochemical cell was made of a recrystallized alumina cylinder of 99.8% purity, obtained from McDanel Co., with a capacity of about 90 cm³. The working electrode was made of a submerged gold flag (0.0025 cm

thick), and a geometrical area of one square centimeter, was connected to the gold current collector (0.05 cm diameter) by a thin gold wire to minimize the meniscus effect (46, 72) because the presence of a meniscus modifies the electrochemical response considerably (73). The counter electrode consisted of a large gold foil which was used as an inner liner of the cell to ensure uniform current distribution. The reference electrode was also a gold foil, but encased in an alumina tube which was pressed against the bottom of the electrochemical cell. The Puratronic grade (99.99%) gold foils and wires were obtained from Johnson Matthey/ÆSAR Group.

Digital mass flow controllers/meters manufactured by Teledyne-Hastings Raydist were used to provide the gas mixtures of the desired compositions of O_2 , CO_2 and Ar, with high precision ($\pm 1\%$ Full Scale). The high purity gases were obtained from Matheson Gas Products and the traces of water were removed by passing the blended gas through a column of 5 Å molecular sieves and Drierite (Fisher Scientific). The gas mixture was bubbled into the melt in the vicinity of the working electrode at a flow rate of about $50 \text{ cm}^3 \text{ min}^{-1}$ through a long alumina tube with four pinholes to form smaller bubbles for enhanced mass transfer. The composition of the gas mixture supplied to the reference electrode compartment was the same as the one used for the working electrode, but at a flow rate of about $5 \text{ cm}^3 \text{ min}^{-1}$.

The electrochemical cell was suspended from a stainless steel header using alumina tubings and an alumina bottom plate connected by the gold wires. Several pierced alumina baffles with spacers were used to decrease the convective heat transfer in order to minimize the temperature gradient within the cell. Also a three-zone furnace, with individual microprocessor-based controllers (Applied Test systems, Inc.), was used to ensure uniform temperature distribution in the cell. The cell temperature was monitored by a Chromel-Alumel thermocouple (Omega), enclosed in a closed end alumina tube, which was firmly pressed against the bottom of the cell. The electrochemical cell and the hanging assembly were enclosed in an outer alumina jacket, held by the header using an "O" ring so that the electrochemical cell assembly was hermetically sealed. The stainless steel header also had a cooling coil to protect the "O" rings.

High purity (99.999%) lithium carbonate (Alfa Products) was carefully weighed in an alumina crucible and the electrochemical cell assembly was slowly heated (50°C/hr) to 350°C under an inert (argon) environment. The electrochemical cell assembly was dried at 350°C in a carbon dioxide environment for 24 hours before heating to 750°C .

The data acquisition setup, which consisted of a potentiostat/galvanostat (PAR Model 273), lock-in-amplifier (PAR Model 5301A), personal computer (IBM PS/2), and software (PAR Headstart and Model 378), supplied by EG&G Princeton Applied Research, was used for cyclic voltammetry and electrochemical impedance measurements. A wide range of frequency, i.e. 0.05 Hz to 10 kHz, was used for the small signal perturbation to determine the capacitive effect attributed to the double layer which is significant at high frequency and the mass transfer related (Warburg) impedance which is dominant at low frequency.

The impedance measurements for frequencies higher than 5 Hz were carried out using the Phase Sensitive Detection (PSD) technique with a lock-in-amplifier and a potentiostat. In the Phase Sensitive Detection technique, the impedances are measured in the frequency domain and the voltage excitation signal is applied simultaneously to the electrochemical cell and a reference channel. The cell response (current signal) is compared with the perturbing signal, using a phase sensitive detector. Usually it is not possible to measure a cell impedance by the PSD technique when the excitation signal frequency is below 1 Hz. Hence, for the perturbation signal of frequency below 5 Hz, the cell impedance was measured by the Fast Fourier Transform (FFT) technique using a personal computer and a potentiostat.

The FFT is a time domain technique in which a digitally generated pseudo-random white noise signal (i.e., the algebraic sum of many individual wave forms of equal amplitude but having a different frequency and phase characteristics) is used as a perturbing signal and the complex response to this signal is resolved by an inverse Fast Fourier Transform into discrete frequency data (82). The FFT technique has a major advantage over frequency domain methods for low frequency

measurement because the data can be obtained considerably faster. The low frequency measurements (below 5 Hz), reported here are for an average of 15 data cycles in order to improve the accuracy of the data by averaging out the noise interference.

The amplitude of a perturbation signal needs to be small to ensure linear response of the electrochemical system, hence decrease the influence of higher harmonics on the measured impedance. The low limit for the amplitude is determined by the signal-to-noise ratio, which can be accepted by the measuring instrument, whereas the high limit is determined by the onset of nonlinear distortion. The impedance spectra for oxygen reduction on gold in lithium carbonate melt at 750°C were obtained as a function of the excitation signal amplitude; it was observed that the effect of amplitude on the impedance spectra was insignificant when the amplitude of the perturbation signal varied from 3 to 9 mV, indicating that the measurements were in the linear domain. All the measurements reported here were obtained with the excitation signal amplitude of 5 mV.

Electrochemical Impedance Measurements and Analyses

The temperature dependence of oxygen reduction reaction in lithium carbonate melt was investigated by electrochemical impedance spectroscopy to determine the activation energies of the exchange current density and the Warburg coefficient. The effect of temperature on a plot of phase angle *vs.* $\log \omega$ is shown in Fig. 10. In the high frequency region, all plots converged to a 0° phase angle indicating that the solution resistance becomes dominant. At frequencies below 30 Hz, the phase angle approached -45°, indicating mass transfer impedance was significant. The impedance spectra, obtained as a function of temperature, were analyzed by the CNLS method and the optimized parameters are given in Table 2. The effect of temperature on Z' *vs.* $\omega^{-1/2}$ plot is shown in Fig. 11. In the low frequency region, Fig. 11 shows a linear behavior of Z' *vs.* $\omega^{-1/2}$ plot indicating that the mass transfer impedance is dominant. The Warburg coefficient is proportional to the slope of the lines in Fig. 11. The lines in Fig. 11 indicate that an increase in the temperature decrease the Warburg coefficient.

Fig. 10. Effect of Temperature on Phase Angle vs. log ω Plot for Oxygen Reduction on Gold Electrode in Li_2CO_3 Melt; Working Gas: 9:1 O_2/CO_2 .

Fig. 11. Effect of Temperature on Z' vs. $\omega^{-1/2}$ for O_2 Reduction on Gold in Li_2CO_3 melt; Working Gas: 9:1 O_2/CO_2 ; Curve lines: Experimental Data; Symbols: Model Predictions.

This observation is corroborated, quantitatively, by the estimated parameters shown in Table 4. An increase in temperature from 750 to 850°C caused more than a five fold decrease in the Warburg coefficient, whereas the decrease in the charge transfer resistance was about three fold. The double layer capacity value increased with the increase in temperature; a similar trend was observed when the partial pressure of oxygen was increased, while partial pressure of carbon dioxide was kept constant (95). The increase in double layer capacity with temperature may be due to the formation of a solid oxide film on a gold electrode. The effects of temperature on the entire impedance spectrum can be observed by $\log |Z|$ vs. $\log \omega$ plots in Fig. 12. In the high frequency region, $\log |Z|$ vs. $\log \omega$ plot approached the uncompensated electrolyte resistance, R_s , which is independent of frequency. In the low frequency region, complete relaxation due to the charge transfer process ($R_{ct}C_{dl}$) is not observed due to the Warburg impedance. As shown in Fig. 12, the experimental and model data were in good harmony for the entire frequency range of the experiment.

Since impedance measurements were obtained at the equilibrium potential, in the absence of DC polarization, the Warburg coefficient is expressed by the following equation (81):

$$\sigma = \frac{RT}{n^2 F^2 A \sqrt{2}} \left(\frac{1}{D_O^{1/2} C_O} + \frac{1}{D_R^{1/2} C_R} \right) \quad [79]$$

For oxygen reduction in a lithium carbonate melt, concentration of the peroxide ions (C_O) is much smaller compared to the concentration of the carbonate ions (C_R). Considering that D_O and D_R are of the same order of magnitude, then $1/D_R^{1/2} C_R$ is negligible compared with $1/D_O^{1/2} C_O$. Thus Eqn. [79] can be approximated by the following expression:

$$\sigma = \frac{RT}{n^2 F^2 A \sqrt{2}} \left(\frac{1}{D_O^{1/2} C_O} \right) \quad [80]$$

The mass transfer parameter, $D_O^{1/2} C_O$, and the exchange current density values were calculated using Eqns. [80] and [81], respectively.

$$R_{ct} = \frac{RT}{n F i_0} \quad [81]$$

Table 4. Parameters Estimated by Impedance Analysis Using CNLS Program; Gas Composition: 90% O₂ and 10% CO₂; Parameter R_s: Constant Parameter.

Temperature °C	σ $\Omega \text{ cm}^2 \text{ s}^{-1/2}$	R _{ct} $\Omega \text{ cm}^2$	C _{dl} $\mu\text{F cm}^{-2}$	R _s $\Omega \text{ cm}^2$
750	81.3±2.5	0.95±0.48	301±17	0.38
775	49.8±2.0	0.93±0.35	400±26	0.38
800	30.6±1.0	0.68±0.17	506±29	0.38
825	19.2±0.6	0.40±0.10	692±42	0.38
850	13.9±0.3	0.30±0.05	855±44	0.39

Fig. 12. Effect of Temperature on $\log |Z|$ vs. $\log \omega$ Plot for O_2 Reduction on Gold Electrode in Li_2CO_3 Melt; Working Gas: 9:1 O_2/CO_2 ; Symbols: Experimental data; Curve Lines: Model Predictions.

The Arrhenius plot for the exchange current density is shown in Fig. 13, and the activation energy was estimated to be $121.7 \text{ kJ mol}^{-1}$. The apparent activation energy for the mass transfer parameter, $D_O^{1/2}C_O$, was calculated to be about 181 kJ mol^{-1} from the Arrhenius plot for it is shown in Fig. 14. The apparent activation energy for the mass transfer parameter is a sum of the activation energy for the formation of peroxide ions (Eqn. [1]) and one half of the activation energy of its diffusion coefficient. The estimated activation energy value for $D_O^{1/2}C_O$ is very close to that determined by Appleby and Nicholson (46) for oxygen reduction in lithium carbonate melt. Uchida *et al.* (61) examined the effect of temperature on oxygen reduction on a submerged gold electrode in $(\text{Li-K})\text{CO}_3$ and observed a remarkable change in these activation energies with temperature. This change in activation energy with temperature, indicates a shift in the rate controlling mechanism of oxygen reduction. The activation energies determined by Uchida *et al.* (63), in the region of temperature higher than 700°C , were about 110 and 149 kJ/mol for i_o and $D_O^{1/2}C_O$, respectively. These values are close to the values obtained in this work for oxygen reduction in lithium carbonate melt, which is known to proceed via a peroxide mechanism. Also, the study conducted by Uchida *et al.* showed that the activation energies increased with temperature, indicating that the rate controlling mechanism has shifted to an alternate or parallel path. If the rate controlling mechanism had shifted from one of a succession of elementary steps to another in the series, then the activation energy for i_o would decrease with the increase in temperature (96). These results indicated that the oxygen reduction in $(\text{Li-K})\text{CO}_3$ eutectic melt at temperatures higher than 700°C proceeded via peroxide mechanism. The other rate controlling mechanism, for temperatures below 700°C , could be the superoxide mechanism.

Cyclic Voltammetry

Cyclic voltammetry was carried out to study the effect of temperature on oxygen reduction on a submerged gold electrode in lithium carbonate melt for the gas composition of 90% O_2 and 10% CO_2 . The effect of temperature on cyclic voltammogram

Fig. 13. Arrhenius Plot of Exchange Current density, Obtained from Impedance Analysis.

Fig. 14. Arrhenius Plot of $D_O^{1/2} C_O$, determined from Impedance Analysis

for the scan rate of 100 mV/s is shown in Fig. 15. As shown in Fig. 15, an increase in temperature increased the cathodic peak current density. The current densities in the reverse scan were less cathodic than those obtained in the forward scan and there was no peak reversal. When the applied potential returned to the initial potential, a large anodic current was observed which subsided slowly and reached zero in a few minutes. Since the cyclic voltammograms shown in Fig. 15 are for the same scan rate of 100 mV/s, the area under the cathodic sweep represents the charge passed during the forward sweep. A plot of the anodic current density, observed at the end of the sweep, *vs.* the charge passed in the forward sweep showed a linear behavior with a slope of about 0.5, when the potential scan rate was kept constant at 100 mV/s and temperature was varied from 750°C to 850°C. Lu (23) made a similar observation for oxygen reduction on gold in a eutectic mixture of lithium carbonate and potassium carbonate. He attributed this behavior to the local accumulation of unneutralized oxide ions which shifts the reversible electrode potential in the negative direction. As suggested by Borucka (42), the reversible electrode ($O_2, CO_2/CO_3^{2-}$) potential may depend on the local activity of oxide ion at the electrode-electrolyte interface:

$$E_{O_2, CO_2/CO_3^{2-}} = E_{O_2/O^{2-}}^{\circ} + \frac{RT}{2F} \ln \left(\frac{P_{O_2}^{1/2}}{a_{O^{2-}}} \right) \quad [82]$$

where

$$E_{O_2/O^{2-}}^{\circ} = E_{O_2, CO_2/CO_3^{2-}}^{\circ} + \frac{RT}{2F} \ln K_d \quad [83]$$

Lu and Selman (97) showed that oxygen electrode potential shifts in the negative direction by the addition of lithium oxide to the melt. As shown in Fig. 15, the peak potential was about 45-50 mV negative to the reversible potential, which corresponded to RT/nF ($n=2$ for peroxide reduction). The peak current density *vs.* square root of the scan rate plots for various temperatures are shown in Fig. 16. The linear behavior of i_p *vs.* $v^{1/2}$ plots, shown in Fig. 16, and invariance of E_p with respect the scan rate (up to 200 mV/s) indicates that oxygen reduction in lithium carbonate melt is as fast kinetics (79). Similar behavior was observed by Lu (23) and Uchida *et al.* (31) in the eutectic mixture of lithium carbonate and potassium carbonate. The slope

Fig. 15. Effect of Temperature on Cyclic Voltammogram for O₂ Reduction; Reference and Working Gases Have Same Composition.

of i_p vs. $v^{1/2}$ plot is proportional to the concentration of the diffusing species. As suggested by Appleby and Nicholson (2), the diffusion-limited peak for O_2 reduction in Li_2CO_3 can be described by the theory developed by Berzins and Delahay (76) for the reversible diffusion controlled peak where the product activity is considered to be invariant and equal to unity (e.g., metal deposition) because the final product of the oxygen reduction in molten carbonate is the carbonate ion (Eqn. [25]). The expression for the peak current density is similar to the one for the polarographic case, except the numerical coefficient is different. The proportionality between the peak current density and the concentration of the diffusing species is given below:

$$i_p = 0.61(nF/RT)^{1/2} nFD_O^{1/2} C_O v^{1/2} \quad [84]$$

The mass transfer parameter, $D_O^{1/2} C_O$, was calculated from the slope of i_p vs. $v^{1/2}$ plot by using Eqn. [84]. As shown in Table 5, the values of $D_O^{1/2} C_O$ obtained by cyclic voltammetry concurred well with those estimated by the electrochemical impedance spectroscopy. The product, $D_O^{1/2} C_O$, increased with the increase in temperature which is partly due to the increase in peroxide ion concentration. The apparent activation energy for $D_O^{1/2} C_O$ obtained by cyclic voltammetry was about 170 kJ/mole, which is consistent with the value obtained by electrochemical impedance spectroscopy.

Conclusions

The oxygen reduction reaction on a submerged gold electrode in a pure lithium carbonate melt was examined by electrochemical impedance spectroscopy and cyclic voltammetry techniques. The impedance spectra were analyzed by the complex nonlinear least square method to determine the kinetic and mass transfer parameters such as the charge transfer resistance, Warburg coefficient, double layer capacity, etc. The apparent activation energies for the exchange current density and mass transfer parameter, $D_O^{1/2} C_O$, were determined to be 122 and 175 kJ/mol, respectively. The mass transfer parameters estimated by electrochemical impedance spectroscopy and cyclic voltammetry techniques showed good agreement.

Fig. 16. Effect of Temperature on i_p vs. $v^{1/2}$ for O_2 Reduction on Gold Electrode in Li_2CO_3 melt; working gas: 9:1 O_2/CO_2 ; Reference gas: 9:1 O_2/CO_2

Table 5. Comparison of Product, $D_O^{1/2}C_O$, Estimated by Cyclic Voltammetry and Impedance Analysis; Gas Composition: 90% O_2 and 10% CO_2 .

Temperature °C	$D_O^{1/2}C_O \times 10^9$ $\text{molcm}^{-2}\text{s}^{-1/2}$	
	Cyclic Voltammetry	Impedance Analysis
750	2.09	1.99 ± 0.03
775	3.50	3.33 ± 0.06
800	5.73	5.53 ± 0.09
825	8.70	9.01 ± 0.13
850	12.14	12.70 ± 0.14

CHAPTER V

EFFECTS OF PARTIAL PRESSURE OF OXYGEN

Introduction

An elucidation of the oxygen reduction reaction in molten alkali carbonate is essential because overpotential losses in the molten carbonate fuel cell are considerably greater at the oxygen cathode than at the hydrogen anode. Appleby and Nicholson (46) examined the oxygen reduction reaction in molten carbonates on a submerged gold electrode, using steady state and potential scan techniques. They observed that oxygen dissolves chemically in molten carbonate as peroxide or superoxide ions depending on the cations present in the melt. In pure Li_2CO_3 and Li-rich melts, the peroxide species is dominant, whereas in a K-rich melts the superoxide species is dominant. Hence, the oxygen reduction mechanism strongly depends on the cations present in the melt. Lu (23) investigated the oxygen reduction process in pure Li_2CO_3 and in a Li-K (62 mol%:38 mol%) carbonate eutectic mixture using the potential step method. The exchange current density, determined by Lu (39 mA/cm^2 for 90% O_2 and 10% CO_2 at 750°C in Li_2CO_3 melt), is two orders of magnitude higher than that observed by Appleby and Nicholson (0.34 mA/cm^2), who used the potential scan technique. Lu concluded that the exchange current densities, determined from the potential scan data underestimate the actual values. Uchida et al. (61, 63) determined the kinetic parameters of oxygen reduction in a Li-K (42.7 mol%:57.3 mol%) carbonate eutectic melt on a gold electrode using impedance analysis, potential step and coulometric relaxation methods. They found that the exchange current density was about the same order of magnitude as that observed by Lu. In addition, they concluded that impedance analysis is the most reliable of the three methods for the determination of the kinetic parameters for oxygen reduction in molten carbonates. These studies make it clear that the mechanism of the oxygen reduction in molten carbonate is not well understood. Consequently in the present

work, the kinetic and transport parameters are determined as a function of P_{O_2} and temperature using cyclic voltammetry and impedance analysis.

Experimental

The experimental arrangement and the electrochemical cell assembly used in this work have been described in Chapter III. The working electrode was made of a submerged gold flag (0.025 mm thick), with a geometrical area of one square centimeter, connected to the gold current collector (0.5 mm diameter) by a thin gold wire to minimize the meniscus effect (72). The counter electrode consisted of a large gold foil, which was used as an inner liner of the cell to ensure uniform current distribution. The reference electrode was also made of a gold foil, but encased in an alumina tube which was pressed against the bottom of the electrochemical cell. The high purity (99.9%) gold foils and wires were obtained from Johnson Matthey/ÆSAR Group. Digital mass flow controllers/meters manufactured by Teledyne-Hastings Raydist were used to provide the gas mixtures of the desired compositions (O_2 , CO_2 and Ar) with high precision ($\pm 1\%$ full scale). The high purity gases were obtained from Matheson Gas Products and the traces of water were removed by passing the blended gas through a column of 5 Å molecular sieves and Drierite (Fisher Scientific). The gas mixture was bubbled into the melt in the vicinity of the working electrode at a flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$ by a long alumina tube with four holes. The composition of the gas mixture supplied to the reference electrode compartment was the same as the one used for the working electrode, but at a flow rate of $5 \text{ cm}^3 \text{ min}^{-1}$. The equilibrium between the gas and the carbonate melt was achieved by bubbling the gas for at least 12 hours prior to the experiment. For this study, P_{O_2} was varied from 0.1 to 0.8 atm., while P_{CO_2} was kept constant at 0.2 atm. The total pressure was kept constant at 1 atm. by varying the partial pressure of argon. The Puratronic grade (99.999%) lithium carbonate (Alfa Products) was carefully weighed in an alumina crucible (90 ml capacity) and the electrochemical cell was slowly heated (50°C/hr) to 350°C under inert environment. The electrochemical cell assembly was dried at 350°C in a

carbon dioxide environment for 24 hours before heating to 800 °C. The data acquisition set-up consisted of a potentiostat/galvanostat (Model 273), lock-in-amplifier (Model 5301A), personal computer (IBM PS/2), and software (Model 378) supplied by EG&G PAR.

Cyclic Voltammetry

Cyclic voltammetry measurements were made for oxygen reduction on a gold electrode in a quiescent Li_2CO_3 melt as a function of scan rate, temperature, and P_{O_2} . The working electrode potential was scanned between the rest potential and -0.5 V *vs.* reference electrode; the scan rate was varied from 10 to 200 mV/s. The effect of P_{O_2} on the cyclic voltammogram, recorded at the scan rate of 100 mV/s at 800°C temperature is shown in Fig.17. During the forward scan, a diffusion-limited peak, followed by a limiting plateau, was observed. The peak potential (E_p) was found to be independent of the scan rate (up to 200 mV/s) and the position of this peak was 40-45 mV negative to the rest potential. Appleby and Nicholson (46) made a similar observation and attributed it to peroxide reduction in a Li_2CO_3 melt, as shown in the following mechanism:

The overall reaction is

where (O^-) is a transient species. In this study, it was concluded that the first charge transfer reaction (Eqn. [86]) is the rate determining step for an immersed electrode. The current densities in the reverse scan were lower than those in the forward scan

Fig. 17. Effect of P_{O_2} on Cyclic Voltammogram for O_2 Reduction at 800°C ; Reference and Working Gases Have Same Composition.

and at the end of the cycle, large anodic current densities, which subsided slowly and reached zero in a few minutes, were observed. Lu (23) observed similar behavior for O_2 reduction in Li-K melt and attributed it to an increase in the basicity of the melt near the working electrode due to an accumulation of oxide ions produced during the forward sweep, which shifts the equilibrium potential in the negative direction.

A plot of the effect of P_{O_2} on the peak current density (i_p) vs. square root of the scan rate ($v^{1/2}$) at 800°C is shown in Fig. 18. The linear behavior of i_p vs. $v^{1/2}$, shown in Fig. 18, and the invariance of E_p with respect to the scan rate (Fig. 17) indicate that oxygen reduction in a Li_2CO_3 melt is reversible up to 200 mV/s (79). As shown in Fig. 18, an increase in partial pressure of oxygen increases the slope of the i_p vs. $v^{1/2}$ plot. As suggested by Appleby and Nicholson (46), the diffusion-limited peak for O_2 reduction in Li_2CO_3 can be described by the theory developed by Berzins and Delahay (76) for the reversible diffusion controlled peak where the product activity is considered to be invariant and equal to unity (e.g. metal deposition). According to Berzins and Delahay, the peak current density is given by the following expression:

$$i_p = 0.61 \frac{(nF)^{3/2}}{(RT)^{1/2}} C_O D_O^{1/2} v^{1/2} \quad [90]$$

The transport parameter $D_O^{1/2} C_O$ was calculated from the slope of i_p vs. $v^{1/2}$ plot using Eqn. [90]. The calculated values of this transport parameter for various P_{O_2} are given in Table 6. Increase in partial pressure of oxygen increased the product $D_O^{1/2} C_O$, mainly due to increase in peroxide ion concentration. Plots of the effect of P_{O_2} on the cyclic voltammogram and on the i_p vs. $v^{1/2}$ plots at 850°C are shown in Figs. 19 and 20 respectively; estimated values of $D_O^{1/2} C_O$ are given in Table 6. The temperature change caused a two fold increase in $D_O^{1/2} C_O$. Reaction order plots for $D_O^{1/2} C_O$ with respect to P_{O_2} , at constant P_{CO_2} , are shown in Fig. 21. The O_2 reaction order obtained by linear regression analysis is close to $+0.5$, which agreed well with the peroxide formation step (Eqn. [85]) in the reaction mechanism described earlier.

Fig. 18. Effect of P_{O_2} on i_p vs. $v^{1/2}$ Plot for O_2 Reduction on Gold Electrode in Li_2CO_3 Melt at 0.2 atm P_{CO_2} and 800°C; Symbols: Experimental Data; Lines: Regression Data.

Fig. 19. Effect of P_{O_2} on Cyclic Voltammogram for O_2 Reduction at 850°C ; Reference and Working Gases Have Same Composition.

Fig. 20. Effect of P_{O_2} on i_p vs. $v^{1/2}$ Plot for O_2 Reduction on Gold Electrode in Li_2CO_3 Melt at 0.2 atm. P_{CO_2} and 850°C; Symbols: Experimental Data; Lines: Regression Data.

Table 6. Influence of P_{O_2} on Product $D_O^{1/2}C_O$ Estimated by Cyclic Voltammetry and Electrochemical Impedance Spectroscopy at 0.2 atm P_{CO_2} .

	$D_O^{1/2}C_O \times 10^9$ $\text{mol cm}^{-2} \text{sec}^{-1/2}$			
Temperature °C	800		850	
P_{O_2} atm	Cyclic Voltammetry	Impedance Analysis	Cyclic Voltammetry	Impedance Analysis
0.1	1.08	1.03 ± 0.04	2.41	2.53 ± 0.06
0.2	1.49	1.49 ± 0.03	3.71	3.08 ± 0.09
0.4	2.07	2.12 ± 0.07	4.95	5.25 ± 0.17
0.6	2.53	2.70 ± 0.09	6.12	6.60 ± 0.22
0.8	2.92	3.08 ± 0.10	7.26	7.65 ± 0.28

Fig. 21. Plots of $\log D_0^{1/2}C_0$ vs. $\log P_{O_2}$ for O_2 Reaction Order Determination at 0.2 atm. P_{CO_2} ; $D_0^{1/2}C_0$ Obtained by Cyclic Voltammetry.

Electrochemical Impedance Measurements and Analyses

The impedance measurements were carried out for oxygen reduction in Li_2CO_3 melt at the rest potential as a function of P_{O_2} , temperature and frequency (0.05 Hz-10 kHz). For frequencies higher than 10 kHz, an inductive behavior (positive imaginary impedance) was observed; hence the high frequency measurements were limited to 10 kHz. Figs. 22 and 23 show the effect of P_{O_2} on the Bode plot (phase angle vs. $\log \omega$) for 800°C and 850°C respectively. For high frequencies, the phase angle approached 0°, indicating a purely resistive behavior of the impedance. The impedance at 0° phase angle is a measure of the solution resistance (R_s) between the working and reference electrodes. At low frequencies, the phase angle approached -45°, indicating that mass transfer (Warburg) impedance was dominant. The effect of P_{O_2} on oxygen reduction kinetics is evident at intermediate frequencies, reflecting an increase of charge transfer resistance (R_{ct}) with decrease in P_{O_2} . The effect of temperature can be observed by comparison of Figs. 22 and 23; an increase of temperature decreases the charge transfer resistance and the mass transfer resistance became dominant at relatively higher frequencies. The sharp deviations in the data near 110 Hz frequency are due to the measurement system.

A Complex Nonlinear Least Square (CNLS) parameter estimation program (89, 90), based on the Randles-Ershler equivalent circuit (83, 84), was used for the impedance analysis. This analysis provides estimates of the charge transfer resistance (R_{ct}), double layer capacity (C_{dl}), Warburg coefficient (σ), and solution resistance (R_s). In our analysis, we found that the weighting factor (inverse of the error variance) influenced the accuracy of the parameters estimated from the impedance data. Thus in this work, we used a proportional weighting factor (94) to estimate kinetic and mass transfer parameters from the impedance data. Figs. 24 and 25 show the effect of P_{O_2} on real impedance (Z') vs. the inverse square root of angular frequency ($\omega^{-1/2}$) for temperatures 800°C and 850°C, respectively. In a low frequency region, Z' vs. $\omega^{-1/2}$ plots showed a linear behavior with a slope proportional to the Warburg Coefficient (σ). As shown in Figs. 24 and 25, σ decreased with increase in P_{O_2} and temperature.

Fig. 22. Phase Angle vs. $\log \omega$ Plot as a Function of P_{O_2} for O_2 Reduction on Gold Electrode in Li_2CO_3 Melt at 0.2 atm. P_{CO_2} and $800^\circ C$.

Fig. 23. Phase Angle vs. $\log \omega$ Plot as a Function of P_{O_2} for O_2 Reduction on Gold Electrode in Li_2CO_3 Melt at 0.2 atm. P_{CO_2} and $850^\circ C$.

due to an increase in peroxide ion concentration. The curved lines in Figs. 24 and 25 show Z' vs. $\omega^{-1/2}$ plots for the data computed by the model using estimated parameters. The estimated parameters for various partial pressures of oxygen are given in Tables 7 and 8. These tables show that increase in P_{O_2} and temperature decreases R_{ct} and σ , whereas the change in R_s is negligible. The effects of P_{O_2} and temperature on the impedance spectrum can be observed from $\log |Z|$ vs. $\log \omega$ plots shown in Figs. 26 and 27.

Since impedance measurements were obtained at the rest potential, the following expressions can be used for the charge transfer resistance and the Warburg coefficient (80):

$$R_{ct} = \frac{RT}{nFi_0} \quad [91]$$

$$\sigma = \frac{RT}{n^2F^2A\sqrt{2}} \left(\frac{1}{D_O^{1/2}C_O} + \frac{1}{D_R^{1/2}C_R} \right) \quad [92]$$

For peroxide reduction in Li_2CO_3 melt, C_O is much smaller than C_R because the final product is carbonate ion. Therefore $1/D_R^{1/2}C_R$ is negligible compared with $1/D_O^{1/2}C_O$. Thus Eqn. [92] can be approximated by the following expression:

$$\sigma = \frac{RT}{n^2F^2A\sqrt{2}} \left(\frac{1}{D_O^{1/2}C_O} \right) \quad [93]$$

Using Eqn. [91] (where $n=2$, for peroxide reduction), exchange current densities (i_0) calculated for several values of P_{O_2} and temperature, are shown in Tables 7 and 8. The estimated values of the exchange current density are closer to those obtained by Lu (23) and Uchida *et al.* (61) but two orders of magnitude higher than those observed by Appleby and Nicholson (46), who used potential sweep technique. Lu used the potential sweep and potential step techniques to study the oxygen reduction in a Li-K (62 mol%:38 mol%) carbonate eutectic mixture on a gold electrode. He showed that the exchange current densities determined by the potential sweep method underestimated the actual values. The plots of $\log (D_O^{1/2}C_O)$ vs. $\log P_{O_2}$ at two temperatures are shown in Fig. 28. From the slopes of these lines, the reaction orders for oxygen were calculated. At 800°C, the exchange current density yields a

Fig. 24. Effect of P_{O_2} on Z' vs. $\omega^{-1/2}$ Plot for O_2 Reduction on Gold Electrode in Li_2CO_3 Melt at 0.2 atm. P_{CO_2} and 800°C; Symbols: Experimental Data; Lines: Model Data.

Fig. 25. Effect of P_{O_2} on Z' vs. $\omega^{-1/2}$ Plot for O_2 Reduction on Gold Electrode in Li_2CO_3 Melt at 0.2 atm. P_{CO_2} and 850°C; Symbols: Experimental Data; Lines: Model Data.

Table 7. Electrode Kinetic and Mass Transfer Parameters Estimated by Electrochemical Impedance Spectroscopy Technique at 800°C and 0.2 atm P_{CO_2} .

P_{O_2} atm	σ $\Omega \text{ cm}^2 \text{ s}^{-1/2}$	R_{ct} $\Omega \text{ cm}^2$	$i_0 \times 10^3$ A cm^{-2}	$C_{dl} \times 10^6$ F cm^{-2}	R_s $\Omega \text{ cm}^2$
0.1	164.4±6.3	1.79±1.47	25.9±21.3	270.5±14.7	0.35
0.2	114.0±2.5	1.49±0.57	31.1±11.9	292.6±11.0	0.40
0.4	79.8±2.7	1.17±0.52	39.3±17.3	324.3±17.5	0.36
0.6	62.8±2.1	1.07±0.39	43.3±15.7	348.8±18.3	0.37
0.8	55.1±1.9	0.95±0.34	48.7±17.3	366.0±20.8	0.37

Table 8. Electrode Kinetic and Mass Transfer Related Parameters
 Estimated by Electrochemical Impedance Spectroscopy Technique at
 850°C and 0.2 atm P_{CO_2} .

P_{O_2} atm	σ $\Omega \text{ cm}^2 \text{ s}^{-1/2}$	R_{ct} $\Omega \text{ cm}^2$	$i_0 \times 10^3$ A cm^{-2}	$C_{dl} \times 10^6$ F cm^{-2}	R_s $\Omega \text{ cm}^2$
0.1	70.1±1.8	1.17±0.35	41.4±11.7	335.9±14.1	0.35
0.2	57.7±1.6	1.06±0.32	45.7±13.2	381.3±18.8	0.39
0.4	33.8±1.1	0.64±0.19	76.0±21.6	485.0±28.8	0.38
0.6	26.9±0.9	0.57±0.15	85.4±21.7	549.8±33.5	0.37
0.8	23.2±0.8	0.50±0.15	96.2±26.7	615.2±41.9	0.37

Fig. 26. Effect of P_{O_2} on $\log |Z|$ vs. $\log \omega$ Plot for O_2 Reduction on Gold Electrode in Li_2CO_3 Melt at 0.2 atm P_{CO_2} and 800°C; Symbols: Experimental data; Lines: Model Data.

Fig. 27. Effect of P_{O_2} on $\log |Z|$ vs. $\log \omega$ Plot for O_2 Reduction on Gold Electrode in Li_2CO_3 Melt at 0.2 atm. P_{CO_2} and 850°C; Symbols: Experimental data; Lines: Model Data.

positive reaction order of value 0.30 with respect to P_{O_2} , which is consistent with the peroxide reaction mechanism proposed by Appleby and Nicholson (46), when the first charge transfer (Eqn. [86]) is the rate determining step (r.d.s) and the symmetry factor (β) has a value of 0.5. As shown in Tables 7 and 8, the capacitance increases with an increase in P_{O_2} and this increase is more noticeable at higher temperature. The mass transfer parameter $D_O^{1/2}C_O$ was calculated from the expression for the Warburg coefficient (Eqn. [93]). As shown in Table 6, the mass transfer parameters estimated by impedance analysis and cyclic voltammetry techniques are in good agreement. For comparison with the data available in literature, the concentration of peroxide (C_O) was calculated from the mass transfer parameter $D_O^{1/2}C_O$ for the diffusion coefficient of about $1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. As shown in Table 9, the estimated concentrations of peroxide compare well with those determined from the oxygen solubility measurements of Appleby and Van Drunen (56) and Ramaswami (65). The theoretical values of peroxide concentration in pure lithium carbonate melt, estimated from thermodynamic data (22) are much smaller than those determined by experiment. The discrepancy between the theoretical and experimental data is due to large uncertainty involved in the thermodynamic data for the molten alkali carbonates. The plots to determine reaction order with respect to oxygen for the product $D_O^{1/2}C_O$ are shown in Fig. 29. The reaction orders obtained are consistent with those obtained from cyclic voltammetric measurements. As demonstrated in Table 10, the oxygen reaction orders for the peroxide formation and the exchange current density for oxygen reduction, determined by cyclic voltammetric and electrochemical impedance spectroscopic techniques, are compared in good agreement with the theoretical values.

Conclusions

The kinetic and mass transfer related parameters for the oxygen reduction in pure Li_2CO_3 were determined as a function of P_{O_2} and temperature by impedance analysis. The transport parameter $D_O^{1/2}C_O$, obtained by both impedance analysis and by cyclic voltammetry, shows excellent agreement. The oxygen reaction orders,

Fig. 28. Plots of $\log i_0$ vs. $\log P_{O_2}$ for O_2 Reaction Orders Determination at 0.2 atm P_{CO_2} ; Symbols: Experimental Data; Lines: Regression Data.

Fig. 29. Plots of $\log D_0^{1/2}C_0$ vs. $\log P_{O_2}$ for O_2 Reaction Order Determination at 0.2 atm. P_{CO_2} ; $D_0^{1/2}C_0$ Obtained by Impedance Analysis.

Table 9. Comparison of the Peroxide Concentration Determined from $D_O^{1/2}C_O$ Values (for $D_O = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) with Literature Values and Thermodynamic Data at 800°C Temperature and 0.2 atm P_{CO_2} .

	$C_O \times 10^7$ mol cm ⁻³			
P_{O_2} atm	Electrochemical Impedance Spectroscopy	Ramaswami (20)	Appleby and Van Drunen (19)	Thermodynamic Data (21)
0.1	3.41	3.50	2.90	0.72
0.2	4.71	4.95	4.10	1.02
0.4	6.55	7.00	5.80	1.44
0.6	8.53	8.57	7.10	1.76
0.8	9.74	9.89	8.20	2.03

Table 10. The Reaction Order with Respect to Oxygen for the Exchange Current Density and $D_O^{1/2}C_O$ Estimated by Cyclic Voltammetry and Electrochemical Impedance Spectroscopy.

Parameter	Technique	Temperature °C	Estimated O ₂ Reaction Order	Theoretical O ₂ Reaction Order
$D_O^{1/2}C_O$	Electrochemical Impedance Spectroscopy	800	0.53 ± 0.02	0.50
		850	0.56 ± 0.11	
	Cyclic Voltammetry	800	0.48 ± 0.01	
		850	0.51 ± 0.07	
i_0	Electrochemical Impedance Spectroscopy	800	0.30 ± 0.03	0.38
		850	0.44 ± 0.18	

resulting from the mass transfer parameters and the exchange current densities at 800°C, were determined to be 0.5 and 0.30 respectively. These values are consistent with the peroxide reduction mechanism proposed by Appleby and Nicholson.

CHAPTER VI

EFFECTS OF PARTIAL PRESSURE OF CARBON DIOXIDE

Introduction

The oxygen reduction reaction in molten alkali carbonate electrolytes has been studied for the past quarter century because of its vital role in the performance of the molten carbonate fuel cell. Borucka and Sugiyama (43, 44) studied the $O_2/CO_2/Au$ electrode in a ternary (43.5 mol% Li : 31.5 mol% Na : 25.0 mol%) CO_3 eutectic melt in the temperature range of 550-800°C and concluded the following: (i) the effects of the partial pressures of oxygen and carbon dioxide on the equilibrium potential show that the over-all reaction at equilibrium is:

and the equilibrium potential obeys the Nernst equation

$$E_{O_2.CO_2/CO_3^{2-}} = E_{O_2.CO_2/CO_3^{2-}}^0 + \frac{RT}{2F} \ln (P_{O_2}^{1/2} P_{CO_2}): \quad [95]$$

(ii) the micropolarization tests at near-equilibrium indicate that the electrode is under "mixed" control, due to charge transfer and the mass transport processes, even close to the equilibrium potential; and (iii) the exchange density for the electrode reaction (Eqn. [94]) is about 0.1 mA cm^{-2} . Appieby and Nicholson (45, 48) examined the oxygen reduction reaction in molten carbonates on a submerged gold electrode using steady-state and potential-scan techniques. They observed that oxygen reacts with carbonate ions and forms peroxide and/or superoxide ions and the concentrations of these species depend on the cations present in the melt. In a pure Li_2CO_3 or a Li-rich melt the peroxide species is dominant, whereas in a K-rich melt the superoxide species

is dominant. They proposed the following reaction mechanism for oxygen reduction in pure lithium carbonate melt:

The overall reaction is

where (O^-) is a transient species. According to this reaction mechanism, the first charge transfer step (Eqn. [97]) is rate determining for an immersed electrode. Appleby and Nicholson also examined the oxygen reduction in binary (47 mol% Li : 53 mol% K and 43 mol% Na : 57 mol% K) and ternary (43.5 mol% Li : 31.5 mol% Na : 25 mol% K) eutectic in the temperature range of 700-800 °C and concluded that: (i) the electroactive species is not the oxygen molecule; (ii) both peroxide and superoxide ions are present and are reduced in the parallel steps; and (iii) the neutralization of the oxygen ions by carbon dioxide (Eqn. [99]) is slow. Andersen (22) carried out a thermodynamic study on the chemical equilibria in molten alkali carbonate electrolyte and demonstrated the presence of peroxide ions in quenching experiments followed by chemical analysis. Appleby and Van Drunen (56) determined the total solubility of oxygen species (mainly in the form of peroxide and superoxide ions) in molten carbonate electrolyte as a function of temperature using quenching method. Vogel *et al.* (57) studied the (Li-K) CO_3 eutectic melt at 650°C, using a rotating gold electrode and concluded that superoxide is dominant in this melt and the concentration of molecular oxygen in the melt is negligible. Smith *et al.* (58) determined the solubility of oxygen species in (Li-Na-K) CO_3 eutectic melt as a function of gas composition at 650°C using a chemical method. Smith *et al.* concluded that oxygen reacts with (Li-Na-K) CO_3 melt at 650°C to form superoxide ions and the concentration of physically dissolved molecular oxygen is

negligible. Dunks and Stelman (53) studied the oxygen reduction mechanism in a pure sodium carbonate at 900°C using cyclic voltammetric and computer-curve fitting and proposed the existence of percarbonate ions. They also confirmed the presence of superoxide ion in the frozen electrolyte by Electron Spin Resonance (ESR) spectrum at 77 K temperature. Lu (23) investigated oxygen reduction kinetics in pure Li_2CO_3 and a Li-K (62 mol%:38 mol%) carbonate eutectic mixture using the potential step method. The exchange current density, determined by Lu (39 mA/cm^2 for 90% O_2 and 10% CO_2 at 750°C in Li_2CO_3 melt), is two orders of magnitude higher than that reported by Appleby and Nicholson (0.34 mA/cm^2), who used the potential scan technique. But the dependence of oxygen reduction kinetics on partial pressures of oxygen and carbon dioxide observed by Lu could not be explained by any of the mechanism proposed in the literature. Uchida *et al.* (61) determined the electrode kinetic parameters for oxygen reduction on a gold electrode in a (Li-K) CO_3 (42.7 mol%:57.3 mol%) eutectic melt using impedance analysis, potential step, and coulometric relaxation techniques. They found that the exchange current density was about the same order of magnitude as that reported by Lu. In addition, they concluded that of the three methods for the determination of the electrode kinetic parameters for oxygen reduction in molten carbonates, the electrochemical impedance analysis is the most reliable. Uchida *et al.* (62) examined the oxygen reduction mechanism on a lithiated NiO film, deposited on gold, and Sb-doped SnO_2 electrodes in Li-K eutectic melt by impedance spectroscopy and coulometric relaxation techniques. They (63) also determined the temperature dependence of the electrode kinetic and mass transfer related parameters for oxygen reduction on gold in (Li-K) CO_3 . Adamov *et al.* (64) simulated the oxygen reduction reaction in various alkali carbonate melts: this mathematical model considered the simultaneous presence of peroxide and superoxide ions with slow neutralization reaction. Ramaswami (65) used a rotating disk electrode made of gold to study the oxygen reduction reaction in a pure lithium carbonate melt at 800°C, and determined the diffusion coefficient and peroxide ion concentration as a function of the partial pressure of oxygen.

Even though these studies have yielded valuable information, the mechanism of oxygen reduction in molten carbonate is still not well understood; furthermore, some of the results reported in the literature are not consistent. Previous studies (22, 46, 56, 58) show that the presence of physically dissolved molecular oxygen in molten carbonate electrolyte is insignificant. This is true because oxygen reacts with the molten alkali carbonates to form peroxide and/or superoxide ions, the concentrations of which depend on the cations present in the melt. Thermodynamic data (22) indicate that the equilibrium concentration of the superoxide ion decreases with a decrease in the ionic radii of the alkali cations (i.e., O_2^- decreases in the order $K_2CO_3 > Na_2CO_3 > Li_2CO_3$), and in a pure lithium carbonate melt the superoxide ion is unstable. Consequently, in this work, we have used a pure lithium carbonate melt to avoid the complexity of simultaneous existence of peroxide and superoxide ions. The effects of the partial pressure of oxygen and temperature on electrode kinetics and mass transfer parameters for oxygen reduction in pure lithium carbonate melt were described in the previous chapters. In this chapter, the influence of partial pressure of carbon dioxide on the oxygen reduction kinetics was investigated using electrochemical impedance spectroscopy (EIS) and cyclic voltammetry. Also, the temperature dependence of oxygen reduction kinetics was examined.

Experimental

The experimental setup for high temperature electrode kinetic study and methodology are as described in Chapter III. The working electrode was made of a submerged gold flange (0.025 mm thick), with a geometrical area of one square centimeter, connected to the gold current collector (0.5 mm diameter) by a thin gold wire to minimize the meniscus effect (46, 65, 72). The counter electrode was a large gold foil circumscribing the working electrode to ensure uniform current distribution. The reference electrode was also made of a gold foil, but encased in an alumina tube which was pressed against the bottom of the electrochemical cell. The high purity (99.9%) gold foils and wires were obtained from Johnson Matthey/ESAR Group.

Digital mass flow controllers/meters manufactured by Teledyne-Hastings Ray-
not were used to provide the gas mixtures of the desired compositions (O_2 , CO_2 , and
Ar) with high precision ($\pm 1\%$ Full Scale). The high purity gases were obtained from
Matheson Gas Products and the traces of water were removed by passing the blended
gas through a column of 5 Å molecular sieves and Drierite (Fisher Scientific). The gas
mixture was bubbled into the melt in the vicinity of the working electrode at a flow
rate of $50 \text{ cm}^3 \text{ min}^{-1}$ through a long alumina tube with four holes. The composition
of the gas mixture supplied to the reference electrode compartment was the same as
the one used for the working electrode, but at a lower flow rate ($5 \text{ cm}^3 \text{ min}^{-1}$). In this
study, P_{CO_2} was varied from 0.02 to 0.4 atm, while P_{O_2} was maintained constant at
0.6 atm. The total pressure was 1 atm, by varying the partial pressure of argon. The
high purity (99.999%) lithium carbonate (Alfa Products) was carefully weighed in
an alumina crucible (90 ml capacity) and the electrochemical cell was slowly heated
(150°C/hr) to 350°C in an inert environment. The electrochemical cell assembly was
dried at 350°C in a carbon dioxide environment for 24 hours prior to increasing its
temperature to 800°C .

The data acquisition set-up consisting of a potentiostat/galvanostat (Model
273), lock-in-amplifier (Model 5301A), personal computer (IBM PS/2), and software
(Model 378) supplied by EG&G Princeton Applied Research was used for the cyclic
voltammetric and electrochemical impedance spectroscopic experiments. The EIS
measurements were made over a wide range of frequencies (0.05 Hz to 10 kHz) for
the sinusoidal excitation signal (5 mV rms), because the capacitive effect, attributed
to the double layer, is significant at high frequency while the diffusional (Warburg)
impedance is dominant at low frequency. The impedance measurements for frequen-
cies higher than 5 Hz were carried out by the Phase Sensitive Detection (PSD) tech-
nique using the lock-in-amplifier and the potentiostat. For frequencies below 5 Hz, the
impedance was measured by the Fast Fourier Transform (FFT) technique using
the personal computer and potentiostat. The low frequency measurements (below 5
Hz) represent the average values of 15 data cycles, which were necessary to improve

accuracy of the data by averaging out the noise interference. The amplitude of excitation signal was kept at 5 mV to ensure a linear electrochemical response.

Electrochemical Impedance Measurements and Analyses

The impedance spectra, for oxygen reduction on the submerged gold electrode in lithium carbonate melt at the equilibrium potential, were obtained as a function of P_{CO_2} and temperature. As described in the previous chapters, the absence of semicircle in the complex plane impedance plot indicates fast oxygen reduction kinetics (98). In the region of low frequency, the complex plane plot showed a linear behavior with a slope of 45° due to the Warburg impedance (88). The effect of partial pressure of carbon dioxide on the Bode plot, phase angle vs. $\log \omega$, at 30, 800, and $850^\circ C$ are shown in Figs. 30, 31, and 32, respectively. In the high frequency region, the phase angle approached 0° for all plots, indicating a purely resistive behavior of the cell impedance. The impedance at 0° phase angle is a measure of the uncompensated electrolyte resistance, R_s , between the working and the reference electrodes. At frequencies below 30 Hz, the phase angle approached -45° , indicating that the diffusional impedance is significant. The influence of partial pressure of carbon dioxide on oxygen reduction kinetics is evident at the intermediate frequencies, i.e., the charge transfer resistance increases with increase of P_{CO_2} . The sharp deviations in the Bode plots at about 120 Hz ($\log \omega \approx 2.88$) can not be explained at this time. It may be possible that a flaw exists in the experimental equipment.

The impedance spectra were resolved by using the Randles-Ershler equivalent circuit (83, 84) model shown in Fig. 4. The Randles-Ershler equivalent circuit reflects two parallel process occurring at the electrode-electrolyte interface, namely, the double layer charging and the faradaic reaction. The faradaic impedance consists of the charge transfer resistance which is in series with the Warburg (diffusional) impedance. The uncompensated electrolyte resistance between the working and reference electrodes, R_s , is connected in series with the interfacial impedance. A Complex Nonlinear Least Square (CNLS) parameter estimation program (89 - 91), based on Levenberg-Marquardt algorithm, was used to resolve the impedance spectra. In our

Fig. 30. Phase Angle vs. $\log \omega$ Plot as a Function of P_{CO_2} for O_2 Reduction on Gold Electrode in Li_2CO_3 Melt at 0.6 atm. P_{O_2} and $750^\circ C$.

Fig. 31. Phase Angle vs. $\log \omega$ Plot as a Function of P_{CO_2} for O_2 Reduction on Gold Electrode in Li_2CO_3 Melt at 0.6 atm. P_{O_2} and 800°C .

Fig. 32. Phase Angle vs. $\log \omega$ Plot as a Function of P_{CO_2} for O_2 Reduction on Gold Electrode in Li_2CO_3 Melt at 0.6 atm. P_{O_2} and $850^\circ C$.

ysis, we found that the weighting factor (inverse of the error variance) considerably influenced the accuracy of the parameters estimated from the impedance data. we have used the proportional and functional proportional weighting factors to determine the electrode kinetic and the mass transfer parameters. This analysis yields parameters such as the charge transfer resistance, double layer capacity, Warburg coefficient, and uncompensated electrolyte resistance. The parameter estimation by the complex nonlinear least square method also provides the standard deviation of the estimated parameters.

The effects of partial pressure of carbon dioxide on real part of impedance (Z') versus inverse square root of angular frequency ($\omega^{-1/2}$) at 750, 800, 850°C temperatures are shown in Figs. 33, 34, and 35, respectively. In the low frequency region, Z' vs. $\omega^{-1/2}$ plots showed a linear behavior with a slope proportional to the Warburg coefficient (σ). As demonstrated in Figs. 33, 34, and 35, the Warburg coefficient increases with an increase of P_{CO_2} . This result can be rationalized easily because with increase of P_{CO_2} , there is a decrease in the peroxide ion concentration (Eqn. 3) and the Warburg coefficient is inversely proportional to the concentration of the diffusing species. The predicted impedance values in Figs. 33, 34, and 35, calculated using the estimated parameters values given in Tables 11- 13 and theandles-Ershler equivalent circuit model, agree well with the experimental data. The electrode kinetic and mass transfer parameters as function of P_{CO_2} , for temperatures 750, 800 and 850°C, are presented in Tables 11 - 13, respectively. As shown in these tables, a decrease in P_{CO_2} from 0.4 to 0.02 atm caused a ten fold decrease in the magnitude of the Warburg coefficient. A similar trend was observed when the temperature was increased from 750 to 850°C. The charge transfer resistance also decreased with increase in temperature and decrease in partial pressure of carbon dioxide. The double layer capacity for the smooth gold electrode in a pure lithium carbonate melt was much higher than that observed for a smooth electrode in aqueous electrolytes. Also the double layer capacity increased with decrease in P_{CO_2} and this increase was more significant at higher temperature. This dependence of double layer capacity on temperature and on P_{CO_2} cannot be explained completely at

point, but it may be due to the formation of a solid oxide layer on the electrode. The change in the uncompensated electrolyte resistance with temperature and P_{CO_2} is negligible. The effects of partial pressure of carbon dioxide on the plots of $\log |Z|$ vs. $\log \omega$ are shown in Figs. 36, 37, and 38. The $\log |Z|$ vs. $\log \omega$ plots converge to the value of uncompensated electrolyte resistance at high frequencies. In the low frequency region, complete relaxation of the charge transfer process was not observed due to the diffusional impedance. Also, it is evident from Fig. 4 that the experimental data concur with the model predictions for the entire frequency range of the experiment. Since impedance measurements were obtained at the rest potential, the following expressions were used for calculations of the charge transfer resistance and the Warburg coefficient (80):

$$R_{ct} = \frac{RT}{nFi_0} \quad [101]$$

$$\sigma = \frac{RT}{n^2 F^2 A \sqrt{2}} \left(\frac{1}{D_O^{1/2} C_O} + \frac{1}{D_R^{1/2} C_R} \right) \quad [102]$$

For peroxide reduction in Li_2CO_3 melt, C_O is much smaller than C_R because the final product is carbonate ion. Therefore $1/D_R^{1/2} C_R$ is negligible compared with $1/D_O^{1/2} C_O$. Thus Eqn. [102] can be approximated by the following expression:

$$\sigma = \frac{RT}{n^2 F^2 A \sqrt{2}} \left(\frac{1}{D_O^{1/2} C_O} \right) \quad [103]$$

The calculated values of the exchange current density and product, $D_O^{1/2} C_O$, as functions of P_{CO_2} and temperature, are given in Tables 11-14. The increase in partial pressure of carbon dioxide, decreases the electrode kinetics, e.g., the exchange current density decreased more than five fold when the partial pressure of carbon dioxide was increased from 0.02 to 0.4 atm. As shown in Fig. 39, a plot of $\log i_0$ vs. $\log P_{CO_2}$ for different temperatures, showed a linear behavior and the carbon dioxide reaction order was determined to be about -0.52. As shown in Table 15, the theoretical reaction order is -1.25 when the first charge transfer step (Eqn. [97]) is the rate determining step and the symmetry factor β is 0.5. Thus, the reaction order of the exchange current density with respect to carbon dioxide does not agree with the

Fig. 33. Effect of P_{CO_2} on Z vs. $\omega^{-1/2}$ Plot for O_2 Reduction on Gold Electrode in Li_2CO_3 Melt at $0.6 \text{ atm } P_{\text{O}_2}$ and 750°C ; Symbols: Experimental Data; Lines: Model Data.

Fig. 34. Effect of P_{CO_2} on Z' vs. $\omega^{-1/2}$ Plot for O_2 Reduction on Gold Electrode in Li_2CO_3 Melt at $0.6 \text{ atm } P_{O_2}$ and $800^\circ C$; Symbols: Experimental Data; Lines: Model Predictions.

Fig. 35. Effect of P_{CO_2} on Z' vs. $\omega^{-1/2}$ Plot for O_2 Reduction on Gold Electrode in Li_2CO_3 Melt at 0.6 atm P_{O_2} and 850°C; Symbols: Experimental Data; Lines: Model Data.

Table 11. Effect of P_{CO_2} on Electrode Kinetic and Mass Transfer Parameters Estimated by Electrochemical Impedance Spectroscopy at 750°C Temperature and 0.6 atm P_{O_2} .

P_{CO_2} atm	σ $\Omega \text{ cm}^2 \text{ s}^{-1/2}$	R_{ct} $\Omega \text{ cm}^2$	$i_0 \times 10^3$ A cm^{-2}	$C_{dl} \times 10^6$ F cm^{-2}	R_s $\Omega \text{ cm}^2$
0.02	27.2 ± 0.66	0.53 ± 0.06	86.5 ± 19.3	560 ± 27.6	0.51
0.04	47.1 ± 0.85	0.66 ± 0.08	70.1 ± 17.2	395 ± 15.9	0.50
0.08	82.9 ± 2.52	1.07 ± 0.26	43.4 ± 20.5	313 ± 17.0	0.38
0.20	156 ± 9.35	2.67 ± 1.03	17.4 ± 13.1	271 ± 18.5	0.36

Table 12. Effect of P_{CO_2} on Electrode Kinetic and Mass Transfer Parameters Estimated by Electrochemical Impedance Spectroscopy at 800°C Temperature and 0.6 atm P_{O_2} .

P_{CO_2} atm	σ $\Omega \text{ cm}^2 \text{ s}^{-1/2}$	R_{ct} $\Omega \text{ cm}^2$	$i_0 \times 10^3$ A cm^{-2}	$C_{dl} \times 10^6$ F cm^{-2}	R_s $\Omega \text{ cm}^2$
0.02	10.3±0.34	0.25±0.06	187±46.2	1250±83.4	0.50
0.04	18.3±0.52	0.42±0.09	111±24.7	729±41.5	0.53
0.08	31.7±1.06	0.58±0.18	79.4±24.6	509±31.6	0.37
0.20	63.2±1.37	0.84±0.25	55.3±16.8	330±14.1	0.37
0.40	100±4.56	1.43±0.91	32.3±20.5	282±19.3	0.40

Table 13. Effect of P_{CO_2} on Electrode Kinetic and Mass Transfer Parameters Estimated by Electrochemical Impedance Spectroscopy at 850°C Temperature and 0.6 atm P_{O_2} .

P_{CO_2} atm	σ $\Omega \text{ cm}^2 \text{ s}^{-1/2}$	R_{ct} $\Omega \text{ cm}^2$	$i_0 \times 10^3$ A cm^{-2}	$C_{dl} \times 10^6$ F cm^{-2}	R_s $\Omega \text{ cm}^2$
0.02	4.31±0.16	0.14±0.02	337±75.1	3220±225	0.51
0.04	6.88±0.23	0.18±0.02	265±62.3	1880±132	0.59
0.08	13.3±0.30	0.27±0.03	177±32.5	891±48.1	0.39
0.20	27.0±0.57	0.47±0.05	103±20.1	411±23.8	0.37
0.40	46.2±1.65	0.71±0.11	67.8±20.3	390±19.3	0.40

Fig. 36. Effect of P_{CO_2} on $\log |Z|$ vs. $\log \omega$ Plot for O_2 Reduction on Gold Electrode in Li_2CO_3 Melt at $0.6 \text{ atm } P_{\text{O}_2}$ and 750°C ; Symbols: Experimental data; Lines: Model Predictions.

Fig. 38. Effect of P_{CO_2} on $\log |Z|$ vs. $\log \omega$ Plot for O_2 Reduction on Gold Electrode in Li_2CO_3 Melt at 0.6 atm P_{O_2} and 850°C; Symbols: Experimental data; Lines: Model Data.

theoretical value for the above mentioned rate determining step. This discrepancy in the carbon dioxide reaction order then be due to slow kinetics of a homogeneous recombination reaction (Eqn. [99]). The Arrhenius plots for the exchange current density are shown in Fig. 40 for different partial pressures of carbon dioxide and the activation energy was calculated to be 131.8 kJ/mol; this value is consistent with the value obtained in the previous work (99). The plots of $\log D_{\text{O}}^{1/2} \text{CO}$ vs. $\log P_{\text{CO}_2}$ for three different temperatures are shown in Fig. 41 and the value of the reaction order with respect to carbon dioxide calculated from the slopes of these plots is about -0.8. As shown in Table 15, the estimated reaction order for peroxide ions agrees well with the theoretical dependence of peroxide concentration on partial pressure of carbon dioxide. The Arrhenius plots for $D_{\text{O}}^{1/2} \text{CO}$ for four partial pressures of carbon dioxide are shown in Fig. 42; the average value of the apparent activation energy was determined to be 185 kJ/mol.

Cyclic Voltammetry

Cyclic voltammetric measurements were made for oxygen reduction on a gold electrode in a quiescent Li_2CO_3 melt as a function of the scan rate, temperature, and P_{CO_2} . The working electrode potential was scanned between the rest potential (0.0 V) and -0.5 V vs. the potential of the reference electrode; the scan rate was varied from 10 to 200 mV/s. The effects of P_{CO_2} on the cyclic voltammogram, recorded at a scan rate of 100 mV/s and at 750, 800, and 850°C are shown in Figs. 43, 44, and 45, respectively. During the forward scan, a diffusion-limited peak followed by a limiting plateau was observed. The peak potential (E_p) was found to be independent of the scan rate (up to 200 mV/s) and the position of this peak corresponded with $RT/2F$ negative to the rest potential, indicating that two electrons are involved in the oxygen reduction in a pure lithium carbonate melt. As shown in Figs. 43, 44, and 45, an increase in partial pressure of carbon dioxide, decreased the cathodic peak current density. The current densities in the reverse scan were less cathodic than those obtained in the forward sweep. At the end of the sweep, a large anodic current was observed which subsided slowly and reached a zero value in a few minutes. This

Table 14. Comparison of $D_O^{1/2} C_O$ Values Estimated by Cyclic Voltammetry and Electrochemical Impedance Spectroscopy at 0.6 atm P_{O_2} .

Temperature °C	$D_O^{1/2} C_O \times 10^9$ mol cm ⁻² sec ^{-1/2}					
	750		800		850	
	P_{CO_2} atm	Cyclic Voltammetry	Impedance Analysis	Cyclic Voltammetry	Impedance Analysis	Impedance Analysis
0.02		5.67	5.93±0.15	15.6	16.4±0.54	41.1±1.48
0.04		3.32	3.43±0.06	9.24	9.25±0.26	25.8±0.84
0.08		1.92	1.95±0.06	5.07	5.35±0.18	13.3±0.30
0.20		1.06	1.04±0.07	2.53	2.68±0.06	6.60±0.14
0.40		0.68		1.55	1.65±0.07	3.84±0.14

Table 15. The Reaction Orders with Respect to Carbon Dioxide for the Exchange Current Density and $D_O^{1/2}C_O$ Determined by Cyclic Voltammetry and Electrochemical Impedance Spectroscopy.

Parameter	Technique	Temperature °C	Estimated O ₂ Reaction Order	Theoretical O ₂ Reaction Order
$D_O^{1/2}C_O$	Electrochemical Impedance Spectroscopy	750	-0.77 ± 0.08	-1.00
		800	-0.77 ± 0.04	
		850	-0.80 ± 0.06	
	Cyclic Voltammetry	750	-0.71 ± 0.06	
		800	-0.78 ± 0.05	
		850	-0.81 ± 0.08	
i_0	Electrochemical Impedance Spectroscopy	750	-0.50 ± 0.28	-1.25
		800	-0.55 ± 0.13	
		850	-0.52 ± 0.09

Fig. 40. Plots of $\log i_0$ vs. T^{-1} for Activation Energies Determination at 0.6 atm.
 P_{O_2} ; Symbols: Experimental Data; Lines: Model Predictions.

Fig. 41. Plots of $\log D_o^{1/2} C_o$ vs. $\log P_{CO_2}$ for Determination of CO_2 Reaction Orders at 0.6 atm P_{O_2} ; $D_o^{1/2} C_o$ Obtained by Impedance Analysis.

Fig. 42. Plots of $\log D_0^{1/2} C_O$ vs. T^{-1} for Activation Energies Determination at 0.6 atm P_{O_2} ; $D_0^{1/2} C_O$ Obtained by Impedance Analysis.

phenomenon is attributed to the local accumulation of the unneutralized oxide ions which shifts the reversible electrode potential in negative direction (97). The effects of P_{CO_2} on the peak current density (i_p) vs. square root of the scan rate ($v^{1/2}$) plot at 750, 800, and 850°C are shown in Figs. 46, 47, and 48. A linear behavior of i_p vs. $v^{1/2}$ and invariance of E_p with respect to the scan rate indicate that oxygen reduction in Li_2CO_3 melt is "reversible" up to 200 mV/s (79). An increase in partial pressure of carbon dioxide decreases the slope of i_p vs. $v^{1/2}$ plot, because the slope is directly proportional to $D_O^{1/2}C_O$, where D_O is the diffusion coefficient and C_O is the bulk concentration of the diffusion limiting reactant species, peroxide ions. Appleby and Nicholson (46) suggested that the diffusion-controlled peak for O_2 reduction in Li_2CO_3 can be described by the theory developed by Berzins and Delahay (76) for the reversible diffusion controlled peak where the product activity is considered to be invariant and equal to unity (e.g., metal deposition). According to Berzins and Delahay, the peak current density is given by the following expression:

$$i_p = 0.61 \frac{(nF)^{3/2}}{(RT)^{1/2}} C_O D_O^{1/2} v^{1/2} \quad [104]$$

The transport parameter, $D_O^{1/2}C_O$, was calculated from the slope of i_p vs. $v^{1/2}$ plot using Eqn. [104]. As shown in Table 4, the calculated values of the transport parameter for various P_{CO_2} and temperatures are compared with those estimated by the electrochemical impedance spectroscopy. An increase in partial pressure of carbon dioxide decreases the product, $D_O^{1/2}C_O$, which is mainly due to the decrease in peroxide ion concentration. Temperature has a significant effect on the product, $D_O^{1/2}C_O$, for example, at 0.02 atm partial pressure of carbon dioxide, almost an order of magnitude increase in $D_O^{1/2}C_O$ was observed when temperature was increased from 750 to 850°C. However, the influence of temperature on $D_O^{1/2}C_O$ was less significant at higher P_{CO_2} . The reaction order and apparent activation energy for $D_O^{1/2}C_O$, estimated using cyclic voltammetry technique, concurred with those obtained by impedance analysis.

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Fig. 43. Effect of P_{CO_2} on Cyclic Voltammogram for O_2 Reduction at $0.6 \text{ atm } \text{P}_{\text{CO}_2}$ and 750°C ; Reference and Working Gases Have Same composition.

Fig. 44. Effect of P_{CO_2} on Cyclic Voltammogram for O_2 Reduction at $0.6 \text{ atm } P_{O_2}$ and 800°C ; Reference and Working Gases Have Same Composition.

Fig. 45. Effect of P_{CO_2} on Cyclic Voltammogram for O_2 Reduction at $0.6 \text{ atm } P_{\text{CO}_2}$ and 850°C ; Reference and Working Gases Have Same Composition.

Fig. 46. Effect of P_{CO_2} on i_p vs. $v^{1/2}$ Plot for O_2 Reduction on Gold Electrode in Li_2CO_3 Melt at 0.6 atm P_{O_2} and $750^\circ C$.

Fig. 47. Effect of P_{CO_2} on i_p vs. $v^{1/2}$ Plot for O_2 Reduction on Gold Electrode in Li_2CO_3 Melt at 0.6 atm P_{O_2} and 800°C.

Fig. 48. Effect of P_{CO_2} on i_p vs. $v^{1/2}$ Plot for O_2 Reduction on Gold Electrode in Li_2CO_3 Melt at 0.6 atm P_{O_2} and 850°C .

Conclusions

The kinetic and mass transfer related parameters for the oxygen reduction in pure Li_2CO_3 were determined as a function of P_{CO_2} and temperature by electrochemical impedance spectroscopy and cyclic voltammetry. The impedance spectra were analyzed by the Randles-Ershler equivalent circuit model using a complex nonlinear least square parameter estimation technique. The impedance data analysis yielded the electrode kinetic and mass transfer parameters such the charge transfer resistance, Warburg coefficient, double layer capacitance, and uncompensated solution resistance. The influence of carbon dioxide on the Warburg coefficient was examined and its reaction order was estimated to be about -0.8 , which is consistent with the theoretical value of -1.0 for the formation of peroxide species (Eqn. [96]). The values for $D_{\text{O}}^{1/2}\text{CO}$ obtained by impedance analysis and by cyclic voltammetry agree well. The decrease in the exchange current density with increase in partial pressure of carbon dioxide is due to the decrease in the concentration of peroxide ions with an increase in the partial pressure of carbon dioxide (Eqn. [96]). The carbon dioxide reaction order for the exchange current density was determined to be -0.52 . This value does not agree with the predicted theoretical reaction order of -1.25 when the first charge transfer step (Eqn. [97]) is rate determining. This inconsistency in the reaction order may be due to slow neutralization kinetics (Eqn. [99]), since the partial pressure of carbon dioxide was as low as 0.02 atm. The activation energy for the exchange current density was determined to be about 132 kJ/mol. Also, the reaction order with respect to carbon dioxide and the activation energy for $D_{\text{O}}^{1/2}\text{CO}$ were calculated to be -0.8 and 185 kJ/mol respectively.

An examination of a diffusion-controlled peak indicates that the oxygen reduction reaction is "reversible" up to 200 mV/s - the peak potential was found to be independent of the scan rate and the peak current density was proportional to the square root of the scan rate. Since the peak potential was observed to be $RT/2F$ (45 - 50 mV) negative to the equilibrium potential, oxygen reduction involves two electron transfer. The carbon dioxide dependence of the diffusion-controlled peak was determined to be -0.8 . The dependence of the diffusion-controlled peak on partial pressure

of oxygen was determined to be +0.5 by cyclic voltammetry and EIS techniques in the previous chapter. These results clearly indicate that the oxygen reduction reaction on a submerged gold electrode in a pure lithium carbonate is diffusion controlled and the peroxide is the diffusing species. The temperature dependence of the diffusion-controlled peak was also examined and the activation energy was calculated to be about $176.6 \text{ kJ mol}^{-1}$; this activation energy value agrees with that obtained from EIS data.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The oxygen reduction reaction on a fully-submerged gold electrode in a pure lithium carbonate was investigated to determine electrode kinetic and mass transfer parameters. The electrode kinetic and mass transfer parameters were determined using Electrochemical Impedance Spectroscopy (EIS) and cyclic voltammetry. The electrochemical impedance spectra were analyzed using the Randles-Ershler equivalent circuit model and Complex Nonlinear Least Square (CNLS) program to determine the charge transfer resistance, Warburg coefficient, double layer capacity, and uncompensated electrolyte resistance. The electrode kinetic parameters were determined as a function of temperature and partial pressures of oxygen and carbon dioxide to estimate the activation energies and the reaction orders. The estimation of the reaction orders for oxygen carbon dioxide are essential for the determination of oxygen reduction mechanism.

- The literature review indicates that oxygen electrode reaction in molten carbonate electrolyte is very complex. The physical solubility of oxygen in molten alkali carbonate electrolyte is negligible. The chemical equilibria involving oxygen and carbon dioxide form species such as peroxide and superoxide ions which participate in the oxygen reduction mechanism. The concentrations of the peroxide and/or superoxide species depend on the cations present in the melt, temperature, and partial pressures of oxygen and carbon dioxide.
- Cyclic voltammetric measurements were used to "finger print" the oxygen reduction reaction. The cyclic voltammograms showed diffusion-limited peaks followed by limiting current plateaus. The oxygen reduction reaction in a pure lithium carbonate melt is "reversible" up to 200 mV/s.

since a plot the peak current density vs. square root of the scan rate was linear and the peak potential did not change with the scan rate. Also, oxygen reduction reaction in a pure lithium carbonate melt involved two electrons because the peak potential was $RT/2F$ (~ 45 mV) negative to the equilibrium potential.

- The peak current density showed a linear behavior with respect to the square root of the scan rate and the slope of this plot is proportional to the product of the concentration (C_O) and the square root of the diffusion coefficient (D_O) of the limiting species. The product $D_O^{1/2}C_O$ obtained from the cyclic voltammetric measurements agreed well with those obtained by EIS technique. The reaction orders for oxygen and carbon dioxide were determined to be +0.5 and -0.8, respectively; these reaction orders agree with the theoretical reaction orders for formation of peroxide ions.
- The electrochemical impedance spectra indicate that electrode kinetics for oxygen reduction in a pure lithium carbonate melt are very rapid, because of the absence of semicircle in a complex plane impedance plot. The complex plane impedance plot showed a linear behavior with a slope of 45° in a region of low frequency, indicating that the diffusion process is dominant. The electrochemical impedance spectra were analyzed by the complex plane plots (graphical analysis) and CNLS program based on Levenberg-Marquardt algorithm. The electrode kinetic and mass transfer parameters determined by the graphical and CNLS analyses are consistent. The CNLS method uses the entire frequency spectrum, whereas the graphical analysis uses the impedance data in a region of low frequency only. Hence, the parameters estimated by the graphical analysis should be considered approximate compared to those obtained by the CNLS method. The parameters obtained by the CNLS technique not only have better accuracy, but also provide the confidence limits for the estimated parameters.

- The product $D_O^{1/2}C_O$ determined from the values of the Warburg coefficient agreed well with those determined from the cyclic voltammetric measurements. The reaction orders of +0.5 and -0.8 were determined for partial pressures of oxygen and carbon dioxide, respectively. The values of the reaction orders clearly showed that the diffusing species is the peroxide ions. The apparent activation energy of the product $D_O^{1/2}C_O$ was estimated to be 175 kJ/mol; this value is a function of the activation energies of the peroxide formation and the diffusion coefficient.
- The exchange current density values were obtained from the values of the charge transfer resistance. The value of i_0 was estimated to be 44 mA cm⁻² at 750°C and 90% O₂ and 10% CO₂; this value agreed well with the data available in the literature. The reaction order for oxygen was determined to be 0.3-0.4 indicating that the first charge transfer step for the peroxide path may be the rate determining step. The reaction order for carbon dioxide was determined to be -0.5. The apparent activation energy for the exchange current density was estimated to be about 110 kJ/mol; this value of the apparent activation energy agree with that cited in the literature for the (Li,K)₂CO₃ eutectic melt in a region of high temperature.
- The double layer capacitance value increased with a decrease in partial pressure of carbon dioxide and an increase in temperature and partial pressure of oxygen. This behavior indicated formation of an oxide layer on the gold electrode. The uncompensated electrolyte resistance did not show a dependence on temperature, P_{O₂}, or P_{CO₂}.

Recommendations

- Application of the EIS technique to study oxygen reduction kinetics in other melts such as Na₂CO₃, (Li,Na)₂CO₃, (Li,K)₂CO₃, and (Li,Na,K)₂CO₃ for the following objectives: (i) to elucidate oxygen reduction mechanism in other melts, for example, in a potassium-rich melt

the superoxide species may play an important role; (ii) to establish the data base for electrode kinetic and mass transfer parameters; (iii) to determine the effects of additives which are known to promote formation of peroxide/superoxide and/or to suppress the cathode dissolution; and (iv) ultimately, to determine the optimum composition of the electrolyte for the molten carbonate fuel cell.

- Development of a mathematical model based on the phenomenological equations to describe electrochemical impedance spectra for oxygen reduction reaction in molten alkali carbonate electrolytes. The kinetic model should not include an assumption of a single rate determining step.
- The double layer capacitance at a gold electrode in a pure lithium carbonate has a high value and shows a strong dependence on temperature, P_{O_2} , and P_{CO_2} . This behavior requires further investigation.

LIST OF SYMBOLS

a	reaction order for oxygen
$a_{O^{2-}}$	activity of oxide
$a_{CO_3^{2-}}$	activity of carbonate
A	electrode area, cm^2
b	reaction order for carbon dioxide
C_{dl}	double layer capacitance, $\mu\text{F}/\text{cm}^2$
C_j	bulk concentration of species j , mol/cm^3
D_j	bulk diffusion coefficient of species j , cm^2/s
E	electrode potential, V
E°	standard electrode potential, V
E_{appl}	applied electrode potential, V
F	Faraday's constant, $96,487 \text{ C}/\text{equiv.}$
f	objective function for minimization, $\Omega \text{ cm}^2$
i	current density, A/cm^2
i_c	charging current density, A/cm^2
i_f	faradaic current density, A/cm^2
i_o	exchange current density, A/cm^2
i_o^c	kinetic parameter, A/cm^2
i_p	peak current density, A/cm^2
K_d	dissociation constant, atm
n	number of electrons transferred in electrode reaction
N	total number of observation
P_{O_2}	partial pressure of oxygen
P_{CO_2}	partial pressure of carbon dioxide
R	universal gas constant, $8.3143 \text{ J mol}^{-1} \text{ K}^{-1}$
R_{ct}	charge transfer resistance, $\Omega \text{ cm}^2$
R_s	electrolyte resistance, $\Omega \text{ cm}^2$
T	temperature, K

V	electrode potential relative to given reference electrode placed just outside double layer, V
$\tilde{V}$	sinusoidal potential perturbation, V
$ \tilde{V} $	amplitude of the potential perturbation, V
v	scan rate, V/s
w	weighting factor
X	vector of model parameters
Y_{el}	interfacial admittance, $\Omega^{-1}\text{cm}^{-2}$
Z	impedance, $\Omega\text{ cm}^2$
$ Z $	modulus of impedance, $\Omega\text{ cm}^2$
z_i	charge number of species i
Z_W	complex Warburg impedance, $\Omega\text{ cm}^2$

Greek letters

α_a	anodic transfer coefficient
α_c	cathodic transfer coefficient
β	symmetry factor for electrochemical reaction
λ	dummy variable
σ	Warburg coefficient, $\Omega\text{ cm}^2\text{ s}^{-1/2}$
Φ	current function
ϕ	phase angle

Superscripts

	real part
	imaginary part

Subscripts

	n th measurement point
	peroxide or superoxide ions
	carbonate ions

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APPENDIX A

DERIVATION OF ELECTRODE KINETIC EXPRESSIONS

The electrode kinetic expressions, which include theoretical reaction orders and transfer coefficients for oxygen reduction in molten alkali carbonate electrolytes, are derived for different reaction mechanisms. The reaction mechanisms consider the oxyanions such as peroxide (46), superoxide (47, 48), and percarbonate (53) ions. As shown below for the peroxide mechanism, each reaction mechanism is assumed to proceed by a sequence of elementary steps.

Peroxide Path

Overall Reaction

where (O^-) is a transient species.

The electrode kinetic expressions are derived with the following assumptions (64): (i) only one of the elementary steps is considered to be the rate determining step and the other elementary steps are in quasi-equilibrium; (ii) the coverage of the electrode surface by an adsorbed species is negligible; (iii) effects of the double layer on the electrode kinetics are insignificant; (iv) activity of the carbonate ions is invariant and equal to unity; and (v) molten alkali carbonate is considered to be an ideal solution. The electrode kinetic expressions are derived by following the procedures for multistep reactions suggested by Newman (100), Vetter (101), and

Bockris and Reddy (102). According to Newman (100), an elementary step can be represented by the general equation

$$\sum_i s_i M_i^{z_i} = n e^- \quad [110]$$

where, n is the number of electrons transferred and z_i is the charge number of species i . The kinetic expression for the elementary step is given by the following expression:

$$\begin{aligned} r &= \frac{i}{nF} \\ &= k_a \exp \left[\frac{(1 - \beta) nF}{RT} V \right] \prod_i C_i^{p_i} \\ &\quad - k_c \exp \left[\frac{-\beta nF}{RT} V \right] \prod_i C_i^{q_i} \end{aligned} \quad [111]$$

where, β is a symmetry factor, V is the difference in potential between that of the electrode and the solution just outside the double layer, k_a and k_c are the rate constants, and p_i and q_i are the reaction orders in the anodic and cathodic directions, respectively. For the elementary step which does not involve charge transfer, n is zero, otherwise it is unity since multiple electron transfers are improbable in an elementary step. The rate expressions for the elementary steps of the peroxide mechanism are given below:

$$r_1 = k_{a1} C_{O_2^-} P_{CO_2} - k_{c1} P_{O_2}^{1/2} \quad [112]$$

$$\begin{aligned} r_2 &= \frac{i_2}{F} \\ &= k_{a2} C_{(O^-)} C_{O_2^-} \exp \left[\frac{(1 - \beta_2) F}{RT} V \right] - k_{c2} C_{O_2^-} \exp \left[\frac{-\beta_2 F}{RT} V \right] \end{aligned} \quad [113]$$

$$\begin{aligned} r_3 &= \frac{i_3}{F} \\ &= k_{a3} \exp \left[\frac{(1 - \beta_3) F}{RT} V \right] - k_{c3} C_{(O^-)} P_{CO_2} \exp \left[\frac{-\beta_3 F}{RT} V \right] \end{aligned} \quad [114]$$

$$r_4 = k_{a4} - k_{c4} C_{O_2^-} P_{CO_2} \quad [115]$$

With the assumption that the rates of the elementary steps of a simple reaction are always proportional to one another, total current density i is expressed as the follow:

$$i = i_2 = i_3 = 2i_1 = 2i_4 \quad [116]$$

The current density can also be given by the Butler-Volmer equation as function of the surface overpotential and the composition at the electrode surface:

$$i = i_0 \left[\exp \left(\frac{\alpha_a F}{RT} \eta_s \right) - \exp \left(\frac{\alpha_c F}{RT} \eta_s \right) \right] \quad [117]$$

where, α_a and α_c are the anodic and the cathodic transfer coefficients, respectively, and surface overpotential is

$$\eta_s = V - V_0 \quad [118]$$

Rate Determining Step : Eqn. [106]

The steps represented by Eqns. [105], [107], and [108] are in equilibrium, hence r_1 , r_3 , and r_4 are equated to zero to obtain expressions for $C_{O_2^{2-}}$, $C_{(O^-)}$, and $C_{O^{2-}}$, respectively:

$$C_{O_2^{2-}} = K_1 P_{O_2}^{1/2} P_{CO_2}^{-1} \quad [119]$$

$$C_{(O^-)} = \frac{1}{K_3} P_{CO_2}^{-1} \exp \left[\frac{F}{RT} V \right] \quad [120]$$

$$C_{O^{2-}} = \frac{1}{K_4} P_{CO_2}^{-1} \quad [121]$$

where,

$$K_i = \frac{k_{ci}}{k_{ai}} \quad [122]$$

Substituting Eqns. [119]-[121], and [116] into Eqn. [113] to get

$$\frac{i}{2F} = \frac{k_{a2}}{K_3 K_4} P_{CO_2}^{-2} \exp \left[\frac{(2 - \beta_2) F}{RT} V \right] - k_{c2} K_1 P_{O_2}^{1/2} P_{CO_2}^{-1} \exp \left[\frac{-\beta_2 F}{RT} V \right] \quad [123]$$

At equilibrium,

$$i = 0 \quad \text{and} \quad V = V_0 \quad [124]$$

and

$$i_0 = 2F \frac{k_{a2}}{K_3 K_4} P_{CO_2}^{-2} \exp \left[\frac{(2 - \beta_2) F}{RT} V_0 \right] \quad [125]$$

$$= 2F k_{c2} K_1 P_{O_2}^{1/2} P_{CO_2}^{-1} \exp \left[\frac{-\beta_2 F}{RT} V_0 \right] \quad [126]$$

Using Eqns. [123] and [124],

$$V_0 = \frac{RT}{2F} \ln \left(\prod_{i=1}^4 K_i P_{O_2}^{1/2} P_{CO_2} \right) \quad [127]$$

Substituting Eqn. [127] into Eqn. [125],

$$i_0 = 2F \frac{k_{a2}}{K_3 K_4} \prod_{i=1}^4 K_i^{(2-\beta_2)/2} P_{O_2}^{(2-\beta_2)/4} P_{CO_2}^{-(2+\beta_2)/2} \quad [128]$$

Eqn. [128] can be also derived by substituting Eqn. [127] into Eqn. [126]. The exchange current density can be given as a function of P_{O_2} and P_{CO_2} :

$$i_0 = i_0^0 P_{O_2}^a P_{CO_2}^b \quad [129]$$

where, i_0^0 is a temperature-dependent kinetic parameter, a is a reaction order for P_{O_2} , and b is a reaction order for P_{CO_2} . Comparison of Eqns. [128] and [129] provides the expressions for the reaction orders:

$$a = \frac{2 - \beta_2}{4} \text{ and } b = -\frac{2 + \beta_2}{2} \quad [130]$$

Substitution of Eqns. [118], [125], [126], and [127] into [123] and comparison with Eqn. [117] provide the transfer coefficients:

$$\alpha_a = 2 - \beta_2 \text{ and } \alpha_c = \beta_2 \quad [131]$$

Rate Determining Step : Eqn. [107]

Eqns. [105], [106], and [108] are in quasi-equilibrium, hence r_1 , r_2 , and r_4 are equated to zero to obtain expressions for $C_{O_2^{2-}}$, $C_{(O^-)}$, and $C_{O_2^-}$, respectively:

$$C_{O_2^{2-}} = K_1 P_{O_2}^{1/2} P_{CO_2}^{-1} \quad [132]$$

$$C_{(O^-)} = K_2 C_{O_2^{2-}}^{-1} C_{O_2^-} \exp \left[-\frac{F}{RT} V \right] \quad [133]$$

$$C_{O_2^-} = \frac{1}{K_4} P_{CO_2}^{-1} \quad [134]$$

Substitute Eqns. [116] and [132]-[134] into [114] to obtain

$$\frac{i}{2F} = k_{a3} \exp \left[\frac{(1 - \beta_3) F V}{RT} \right] - k_{c3} K_1 K_2 K_4 P_{O_2}^{1/2} P_{CO_2} \exp \left[\frac{-(1 + \beta_2) F V}{RT} \right] \quad [135]$$

At equilibrium,

$$i = 0 \quad \text{and} \quad V = V_0 \quad [136]$$

and

$$i_0 = 2F k_{a3} \exp \left[\frac{(1 - \beta_3) F V_0}{RT} \right] \quad [137]$$

$$= 2F k_{c3} K_1 K_2 K_4 P_{O_2}^{1/2} P_{CO_2} \exp \left[-\frac{(1 + \beta_2) F V_0}{RT} \right] \quad [138]$$

Substituting [127] into Eqn. [137],

$$i_0 = 2F k_{a3} \prod_{i=1}^4 K_i^{(1 - \beta_3)/2} P_{O_2}^{(1 - \beta_3)/4} P_{CO_2}^{(1 - \beta_3)/2} \quad [139]$$

As described earlier, expressions for the reaction orders and the transfer coefficients are determined from Eqn. [139]:

$$a = \frac{1 - \beta_3}{4} \quad \text{and} \quad b = \frac{1 - \beta_3}{2} \quad [140]$$

$$\alpha_a = 1 - \beta_3 \quad \text{and} \quad \alpha_c = 1 + \beta_2 \quad [141]$$

Rate Determining Step : Eqn. [108]

Eqns. [105], [106], and [107] are in quasi-equilibrium, hence r_1 , r_2 , and r_3 are equated to zero to obtain expressions for $C_{O_2^-}$, $C_{O^{2-}}$, and $C_{(O^-)}$, respectively:

$$C_{O_2^-} = K_1 P_{O_2}^{1/2} P_{CO_2}^{-1} \quad [142]$$

$$C_{O^{2-}} = K_2 C_{(O^-)}^{-1} C_{O_2^-} \exp \left[-\frac{F}{RT} V \right] \quad [143]$$

$$C_{(O^-)} = \frac{1}{K_3} P_{CO_2}^{-1} \exp \left[\frac{F}{RT} V \right] \quad [144]$$

Substitute Eqns. [116] and [142]-[144] into [115] to obtain

$$\frac{i}{2F} = k_{a4} - k_{c4} \prod_{i=1}^3 K_i P_{O_2}^{1/2} P_{CO_2} \exp \left[-\frac{2F}{RT} V \right] \quad [145]$$

At equilibrium,

$$i = 0 \quad \text{and} \quad V = V_0 \quad [146]$$

and

$$i_0 = 2F k_{a4} \quad [147]$$

$$= 2F k_{c4} \prod_{i=1}^3 K_i P_{O_2}^{1/2} P_{CO_2} \exp \left[-\frac{2F}{RT} V_0 \right] \quad [148]$$

Substituting [127] into Eqn. [148],

$$i_0 = 2F k_{a4} \quad [149]$$

As described earlier, expressions for the reaction orders and the transfer coefficients are determined from Eqn. [145]:

$$a = 0 \quad \text{and} \quad b = 0 \quad [150]$$

$$\alpha_a = 0 \quad \text{and} \quad \alpha_c = 2 \quad [151]$$

The similar procedure was used to determine the reaction orders and the transfer coefficients for the oxygen reduction mechanisms, involving superoxide and percarbonate ions, described below.

Superoxide Path

Overall Reaction.

Percarbonate Path

Overall Reaction

The symmetry factor β represents the fraction of the applied potential which promotes the cathodic reaction. Usually a value of β lies between zero and one, and it has a value of 0.5 for a system which has symmetrical intersection in a "Morse Plot". The reaction orders and the transfer coefficients were calculated for β equal to 0.5 and the values are given in Table 16.

Table 16. Theoretical Reaction Orders for the Exchange Current Density and the Transfer Coefficients for Oxygen Reduction Reaction.

Mechanism	Rate Determining step	a	b	α_a	α_c
Peroxide	1 e ⁻	0.375	-1.25	1.5	0.5
	2 e ⁻	0.125	0.25	0.5	1.5
	Recomb.	0.000	0.00	0.0	2.0
Superoxide	1 e ⁻	0.625	-0.75	2.5	0.5
	2 e ⁻	0.375	-1.25	1.5	1.5
	3 e ⁻	0.125	0.25	0.5	2.5
	Recomb.	0.000	0.00	0.0	3.0
Percarbonate	1 e ⁻	0.375	-0.25	1.5	0.5
	2 e ⁻	0.125	-0.75	0.5	1.5
	Recomb.	0.000	0.00	0.0	2.0

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