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OXYGEN ELECTRODE IN MOLTEN CARBONATE FUEL CELLS

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Abstract

Electrode kinetics of oxygen reduction on gold in molten lithium carbonate was investigated. Steady state cyclic voltammograms were obtained for the peroxide reduction at the gold electrode in Li_2CO_3 melt, results were found to be in good agreement with the data in the literature. Impedance measurements were made as a function of frequency to evaluate the kinetics and mass transfer related parameters. Impedance data were analyzed using a Complex Nonlinear Least Square (CNLS) parameter estimation program and a graphical procedure based upon the Randles-Ershler equivalent circuit. Parameters estimated by both the methods are in good agreement. One of the proposed micro electrodes is a micro ring, which involves a thin gold film positioned tightly between two alumina roots. As an initial study, the stability of gold films, sputter-deposited on alumina substrates, in the Li_2CO_3 melt was determined.

OXYGEN ELECTRODE IN MOLTEN CARBONATE FUEL CELLS

Introduction:

This project focuses on three areas of research:

- Task 1: Construction of High Temperature Equipment
- Task 2: Microelectrode Study of Oxygen Reduction
- Task 3: Computer Modeling of Reactions

This report summarizes the work carried out during this quarter and the proposed work for the next quarter in Tasks 2 and 3.

WORK CARRIED OUT DURING THE REPORTING PERIOD

Task 2: Microelectrode Study of Oxygen Reduction

Prior to initiating the experimental studies with the microelectrode, it was envisaged to be necessary to test the experimental set up with macroelectrodes. For this purpose, peroxide reduction reactions were investigated on a gold flag electrode in molten Li_2CO_3 as a function of temperature and reactant gas composition.

Cyclic Voltammetry

Cyclic voltammetry was carried out in a quiescent Li_2CO_3 melt for the gas composition of 90% O_2 and 10% CO_2 . The steady state voltammograms obtained at 750°C on a gold electrode for various scan rates are shown in Fig. 1. The potential sweeps were carried out between the rest potential of the working electrode and -500 mV vs. the reference electrode (another gold electrode in the same gaseous and electrolyte environment). During the forward scan a diffusion limited peak and a horizontal limiting current plateau were observed. For a Li_2CO_3 melt this behavior is attributed to peroxide reduction reaction (1). The current densities in the reverse scan are lower than those in the forward scan and there is no peak reversal. When the applied potential returned to the initial potential, a large anodic current was observed. The magnitude of this anodic current in the reverse scan increases with the increase in a current in the forward scan. When cyclic voltammetry was performed continuously, the peak current for the second cycle was smaller than that for the first cycle and the peak potential shifted to a more negative potential. After four cycles, a steady state cyclic voltammogram was obtained. The steady state cyclic voltammograms shown in Fig. 1 are average of ten cycles. Similar behavior was observed by S.H. Lee et.

al. (2) for a Li-K melt. As reported earlier (3), an intermediate peak is observed in both forward and reverse scans around -95 mV vs. the reference electrode. This behavior is discussed in detail in a subsequent section. A plot of peak current density vs. (scan rate)^{1/2} indicates that peroxide reduction reaction is reversible up to 200 mV/s scan rate, and diffusion controlled.

Impedance Measurements and Analysis

Impedance data were measured at the open circuit potential for Li₂CO₃ melt as a function of gas composition, temperature and frequency (0.05 - 10 KHz). For a frequency higher than 10 KHz, an inductive behavior (positive imaginary impedance) was observed; hence the high frequency measurements were limited to 10 KHz. Impedance data were analyzed using equivalent circuit method. The equivalent circuit used (Randles-Ershler) for our analysis is shown in Fig. 3. The equations describing real (Z') and imaginary (Z'') impedances for this type of circuit are given below (4).

$$Z' = R_s + \frac{\theta + \sigma/\sqrt{\omega}}{(\sigma\sqrt{\omega} C_{d1} + 1)^2 + \omega^2 C_{d1}^2 (\theta + \sigma/\sqrt{\omega})^2} \quad (1)$$

$$Z'' = \frac{\omega C_{d1} (\theta + \sigma/\sqrt{\omega})^2 + \sigma^2 C_{d1} + \sigma/\sqrt{\omega}}{(\sigma\sqrt{\omega} C_{d1} + 1)^2 + \omega^2 C_{d1}^2 (\theta + \sigma/\sqrt{\omega})^2} \quad (2)$$

where θ = Charge transfer resistance, Ω
 σ = Warburg impedance coefficient $\Omega\text{cm}^2\text{s}^{1/2}$
 C_{d1} = double layer capacity, F/cm²
 R_s = solution resistance, Ω
 ω = angular frequency
 $= 2\pi f, \text{ s}^{-1}$

CNLS Method

A complex nonlinear least square (CNLS) parameter estimation program (Levenberg-Marquardt Algorithm) based on the equivalent circuit model was used for the analysis of the impedance data. This analysis yields parameters such as R_{ct} , C_{d1} , σ , and R_s . When the

impedance is measured at the rest potential, the exchange current density (i_0) can be obtained from the charge transfer resistance (for $n = 2$) by the equation given below.

$$R_{ct} = \frac{RT}{nFi_0} \quad (3)$$

Fig. 4 describes the experimental conditions and the impedance plots for the experimental data and data obtained from the model (using estimated parameters). The estimated parameters are given in Table 1. Impedance plot in Fig. 4 shows that at high frequencies (~ 10 KHz) the plot converges to a real impedance value (R_s), and at frequencies below 30 Hz, a straight line with a slope of 45° indicates that diffusion (Warburg) impedance is dominant.

Graphical Analysis

This method is based upon the application of low frequency and high frequency approximations to impedance expressions (1) and (2).

1. As $\omega \rightarrow \infty$

$$\begin{aligned} Z' &= R_s \\ Z'' &= 0 \end{aligned} \quad (4)$$

2. As $\omega \rightarrow 0$

$$Z' = R_s + R_{ct} + \sigma\omega^{-1/2} \quad (5)$$

$$Z'' = \sigma\omega^{-1/2} + 2\sigma^2C_{dl} \quad (6)$$

Fig. 5 describes the linear behavior of Z' vs. $\omega^{-1/2}$ for the low frequency data (0.1 - 30 Hz) slope of this plot gives the Warburg coefficient (σ).

Elimination of ω between equations (5) and (6) gives

$$Z'' = Z' - R_s - R_{ct} + 2\sigma^2C_{dl} \quad (7)$$

Fig. 6 shows the impedance plot for the low frequency data. In this case,

$$\text{intercept} = -R_s - R_{ct} + 2\sigma^2C_{dl} \quad (8)$$

Equations (1) and (2) can be used to obtain the expressions for real (Y') and imaginary (Y'') admittances. The expression combining Y' and Y'' is given below.

$$Y'' = \frac{Y'}{P + 1} + \omega C_{dl} \quad (9)$$

where $P = \theta\sqrt{\omega} / \sigma$

when $\omega \rightarrow 0$, $P + 1 \rightarrow 1$ and,

$$\frac{Y''}{\omega} = \frac{Y'}{\omega} + C_{dl} \quad (10)$$

Fig. 7 shows the linear behavior of the admittance plot in a low frequency region with a slope of 45°. The double layer capacity is determined from the intercept of this plot. Parameters estimated by using equations (4), (6), (8) and (10) are tabulated in Table 1. Table 1 shows that the parameters (exchange current density, double layer capacity) estimated by the CNLS and graphical methods are in reasonably good agreement (within an order of magnitude). Similar results were observed by I. Uchida et al. (5) for the gold electrode in Li-K melt.

Microelectrode Fabrication

A gold film (5500 Å) was sputter-deposited on an alumina substrate with an intermediate layer of chromium (450 Å). This sample was exposed to molten lithium carbonate environment for five days at 750°C. At the end of the experiment it was found that the film was unstable in this environment. A similar sample exposed to the high temperature environment (750°C) in air showed that film was stable. These observations indicate that the instability of the gold film on alumina is due to the attack by molten carbonate (e.g. dissolution of the chromium layer) rather than the differential thermal expansion coefficients of the metal and ceramic. Several (alumina base) adhesives were investigated for their stability in the molten carbonate environment at 750°C and were also not stable enough to bond the gold film to the substrate.

Impurity Problem

As stated in an earlier section, an intermediate peak, observed in the cyclic voltammetric experiment, may have been due to some impurities in the melt. As shown in Fig. 1, this peak appears in both (forward and reverse) scans, and the peak height increases with the

scan rates. Attempts were made to identify the impurities in the melt by using cyclic voltammetry and X-ray Photoelectron Spectroscopy.

Cyclic Voltammetry

Samples of Li_2CO_3 (as supplied by vender and after use in above molten salt experiments) were dissolved in 2 M H_2SO_4 to yield a 0.1 M solution. Cyclic voltammetry was conducted on a gold electrode in the potential window from 0.1 - 1.6 V vs. DHE. Voltammograms obtained for these two samples were similar and this technique did not provide any information on impurities.

XPS

XPS analysis was conducted on the gold electrode after the experiment in Li_2CO_3 melt; the energy spectrum is shown in Fig. 8. Energy spectra were also obtained on used and unused Li_2CO_3 samples and are shown in Figs. 9 and 10 respectively. These energy spectra do not show a peak for any impurity.

Task 3: Computer Modeling of Reactions

Work carried out under this task is already decribed in Impedance Measurements and Analysis section of Task 2.

PROPOSED WORK DURING NEXT QUARTER

Task 2:

1. Impedance measurements on gold electrode in Li_2CO_3 melt as a function of gas composition and temperature.
2. Further investigation of the stability of ceramic adhesives (including alumina and H_3PO_4 paste) in a molten carbonate environment at 750°C .
3. Fabrication and testing of gold cylindrical microelectrodes.

Task 3:

1. Analysis of impedance data using CNLS method.
2. Simulation of oxygen reduction for microelectrode geometry under transient conditions.

References

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Table 1: Comparison of Kinetic and Mass Transfer Parameters Obtained by Different Methods of Analysis of Impedance Data.

Parameters					
Methods	$i_o(\text{mA/cm}^2)$	$\theta (\Omega\text{cm}^2)$	$C_{dl} (\mu\text{F/cm}^2)$	$\sigma(\Omega\text{cm}^2 \text{s}^{1/2})$	R_s
CNLS	30.0671	1.5089	341.19	80.9704	0.436
Graphical Analysis	10.3961	4.3640	205.8	82.6452	0.3917

Fig. 1. Steady State Cyclic Voltammograms on Au Electrode

Fig. 2. Peak Current Density vs. Square root of Scan Rate

Fig. 3. Randles-Ershler Equivalent Circuit

Fig. 4. Complex Plane Plots for Impedances Measured at the Rest Potential

Fig. 5. Regression Analysis to Estimate Warburg Impedance Factor

Fig. 6. Regression Analysis for the Impedance Plot

Fig. 7. Regression Analysis for the Admittance Plot

XBE
END

RUN: -71N1 / 12-3F-88 REG: 1.001 ST: 0.50 #C: 229 #SW: 3 DuELL: 0.050
BACKGROUND: 50

Fig.8 Energy Spectrum for Li_2CO_3 film on Gold Electrode.

40

RUN: 7140 / 12-SEP-88

REG: 1.001 ST: 0.50 AC: 221 #SIM: 3 DUELL: 0.050

BACKGROUND: 18

Fig.9. Energy Spectrum for used Li_2CO_3 (powdered).

*3B
JHD
RUN: -75N1 / 13-SEP-83 RUN: 1.001 ST: 0.50 #C: 2200 #SW: 3 DWELL: 0.050
BACKGROUND :

Fig. 10. Energy Spectrum for unused Li_2CO_3 (powdered).

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