The Space Shuttles that are launched at the Kennedy Space Center in Florida have on board oxygen-hydrogen fuel cells. These fuel cells are used as a power supply or back-up power supply for most systems on the space shuttle. The oxygen that flows by the cathode in these fuel cells must be extremely pure (99.989%).

Purified oxygen is necessary for the fuel cells for two reasons. The first is to prevent accumulation of inert gases such as argon, krypton, and nitrogen. The activation of the cell is decreased because the active surface of the cathode is occupied by the inert gas, preventing the oxygen from reaching the active area. Since the fuel cell operates at total consumption of oxygen, there is no exhaust. This inert gas accumulation eventually causes the power output of the fuel cell to drop to zero because oxygen cannot react at the cathode.

The second reason that pure oxygen is needed for the fuel-cells on the space shuttle is that the concentration of CO₂, CO and CH₄ in the oxygen feed must be at a minimum. CO₂ will react with the hydroxyl ion in the potassium hydroxide electrolyte to form bicarbonate ion.

\[ \text{CO}_2(\text{g}) + \text{OH}^- + \text{HCO}_3^- \]  \hspace{1cm} (1)
Since the electrolyte has a high pH the bicarbonate ion will immediately react to form potassium bicarbonate and precipitate.

\[
\text{HCO}_3^- + \text{K}^+ + \text{KHCO}_3(s) \text{ (precipitate)}
\]

(2)

The precipitated potassium bicarbonate deactivates the cathode by depositing on the active sites in the catalytic pores. The concentration of CO and CH$_4$ also needs to be minimized because CO and CH$_4$ will be oxidized to form CO$_2$ at the cathode and the previous sequence of reactions will occur.

\[
\text{CO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}_2(g)
\]

(3)

\[
\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)
\]

(4)

NASA at the Kennedy Space Center now obtains 99.989% liquid oxygen by purchasing it from private industry. There are storage problems because of the hot weather, especially during the summer months. When liquid oxygen evaporates, in the storage tanks, krypton and methane will not evaporate with the oxygen and will remain in the liquid phase because
they have higher boiling points than oxygen. The storage tanks need to be vented periodically to relieve the pressure inside the tanks. The gas leaving the tank is oxygen and impurities with higher boiling points than oxygen will remain liquid or solid. After each venting the concentration of impurities in the liquid oxygen will increase, because oxygen has left the liquid phase and the impurities have not. Repetitive venting of the storage tank eventually leads to sub-standard oxygen purity.

NASA at the Kennedy Space Center is seeking a technique for on-site production of fuel-cell-grade oxygen to become independent of the supplier and minimize the storage time of the liquid oxygen. The cryogenic distillation of air to obtain 99.989% oxygen is expensive because the boiling points of argon and oxygen are so close, \(-185.7^\circ C\) and \(-182.9^\circ C\) respectively. Hydrolysis and electrochemical concentration are being considered as practical alternatives.
THEORY

Thermodynamics

The two half cell reactions which occur in the oxygen concentration cell are shown by equations (5) and (6). The reaction at the cathode is exothermic (-79 kcal/(gram mole of O_2)); therefore the cathode will be at a higher temperature than the anode while the cell is operating. The theoretical voltage bias needed to operate the concentrator cell is calculated using the Nernst equation and depends only on the partial pressures of oxygen at the anode and cathode. When breathing air is the feed gas, the partial pressure of oxygen at the cathode is 0.21 atmospheres while the partial pressure of oxygen at the anode is 1.0 atmosphere. The theoretical voltage needed to bias the cell at equilibrium (zero current) can now be calculated using the following equation.

\[
(E - E^\circ) = \frac{RT}{nF} \ln \left( \frac{P_{O_2}(\text{anode})}{P_{O_2}(\text{cathode})} \right)
\]  

(7)

For the four electron reaction mechanism presented in equations (5) and (6), the calculated theoretical voltage is 0.01 volts. The theoretical voltage when propellant-grade oxygen flows by the cathode is approximately zero at
equilibrium conditions. Because the overall reaction occurring at the cathode is the reverse of the anode, one would expect that the voltage needed to bias the cell would be small. Only the oxygen pressure difference on each side of the cell would constitute a need for voltage bias at equilibrium. The actual voltage needed to bias the cell is two orders of magnitude greater than the theoretical open-circuit voltage because of the internal resistance of the concentrator cell as well as the diffusion and activation limitations under current flow.

**Polarization**

Upon application of a potential, with the subsequent flow of current, polarization occurs at the electrode and in the bulk electrolyte. Figure 2 shows the potential distribution between the two electrodes under load. The ohmic and electrode overpotentials are also shown in Figure 2.

The potential drop in a cell is called an overpotential [1] which is the difference between the equilibrium or open-circuit voltage of the cell and the actual voltage of an operating cell

\[ \eta = E - E_e \]  

The overpotential is caused by three kinds of polarization;
Figure 2 Schematic Representation of Potential Gradient of a Concentration Cell in Driven Mode.
ohmic, activation, and concentration.

\[ \eta = \eta_{\text{ohmic}} + \eta_{\text{activation}} + \eta_{\text{concentration}} \]  \hspace{1cm} (9)

The total overpotential for an operating cell is

\[ \eta_0 = -\eta_{\text{cathode}} + \eta_{\text{anode}} \]  \hspace{1cm} (10)

where the cathodic overpotential which is negative and anodic overpotential which is positive each have activation, concentration and ohmic contributions. The ohmic overpotential is caused by the direct IR loss of the cell, where \( R \) is the impedance of the electrodes, electrolyte and matrix. The activation overpotential is caused by the electrode kinetic rate limitations; the concentration overpotential is caused by the reactant and product diffusion limitations to and from the electrodes.

**Ohmic**

Ohmic losses cause the potential drop developed when the polarizing current \( I \) overcomes the resistance of the electrolyte.

\[ R = \frac{I}{rA} \]  \hspace{1cm} (11)

The resistance of the concentrator cell is minimized by
using a high-conductivity electrolyte and minimizing the distance between the anode and cathode by using a very thin asbestos matrix. The concentration gradient of the cell then becomes large because of the shorter distance. Metallic oxides also contribute to the ohmic resistance, therefore the ohmic resistance will vary from cell to cell depending on construction and the amount of metallic oxide present on current collectors and electrodes. The current flowing through the ohmic resistance decays much faster than the other overpotentials; therefore, a current interruption [42] technique utilizing an oscilloscope and a potentiostat can be implemented to measure it.

**Activation**

When diffusion effects at the electrodes are negligible the following form of Butler-Volmer equation can be used to describe the kinetics of the reaction at an electrode. (Bockris and Reddy, 1970)

\[
I = I_o \left( \exp \left( \frac{\alpha F n}{RT} \right) - \exp \left( \frac{-\alpha F n}{RT} \right) \right)
\]

(12)

The Butler-Volmer equation has an anodic and cathodic contribution to the current density \((I)\).

The equilibrium exchange current density \((I_o)\) represents the individual electronation and de-electronation
currents underlying the state of equilibrium of the cell. Exchange current densities vary from one reaction to another and from one electrode material to another by many orders of magnitude, because they reflect the kinetic properties of the interfacial system concerned.

An equilibrium exchange current implies that the net exchange of electrons across the electrode interface is zero. The overpotential is represented by \((\eta)\) and the transfer coefficients by \((\alpha, \alpha')\). One set of parameters \((\alpha, \alpha', I_0)\) incorporated in Equation (12) describe the kinetics at the anode while another set of parameters \((\alpha', \alpha, I_0')\) placed in Equation (12) describe the kinetics at the cathode. If \(I_0 = I_0'\) then only one set of parameters incorporated into Equation (12) is needed to characterize the kinetics of both electrodes because \(\hat{\alpha} = \hat{\alpha}\) and \(\hat{\alpha}' = \hat{\alpha}'\). This implies the reaction mechanism is the same at the anode and cathode. \(I_0 \neq I_0'\) for the oxygen concentrator cell; therefore two sets of parameters are needed to describe the reaction kinetics and the reaction mechanism at the anode and cathode are not identical.

The anodic and cathodic transfer coefficients at each electrode have the following relationship

\[
\hat{\alpha} + \hat{\alpha}' = \frac{N}{V}
\]

where \((N)\) is the total number of electrons that are
transfered and the number of times the rate limiting step occurs in designated as (V). Note that the anodic and cathodic transfer coefficients at the cathode are not necessarily equal to the anodic and cathodic transfer coefficients at the anode.

**Tafel Region**

The Butler-Volmer equation (12), reduces to the Tafel form when the cathodic or anodic contribution is less than 1.0% of the total current. This occurs at overpotentials greater than 100 mV or less than -100 mV. The Tafel forms of the Butler-Volmer equation (12) when the cathodic or anodic contribution is negligible follow.

\[
\eta > 100 \text{mV} \\
\ln(I) = \ln(I_0) + \frac{\alpha F n}{RT} \\
\eta < -100 \text{mV} \\
\ln(I) = \ln(I_1^0) - \frac{\alpha' F n}{RT}
\]

Note that when \( \ln(I) \) versus \( \eta \) is plotted the intercept at the ordinate when \( \eta = 0 \) is \( \ln(I_0) \). The Tafel slope is the slope of the line \( \frac{\alpha F}{RT} \). The exchange current density \( (I_0) \) and a transfer coefficient \( (\alpha) \) for the anode and cathode can be determined from the slopes and intercepts of Tafel plots. Equation (13) allows the \( (I_0) \) and \( (\alpha) \) to be determined for the anode, while Equation (14) allows the \( (I_0') \) and \( (\alpha') \) to
be determined for the cathode.

**Diffusion**

The diffusional or concentration overpotential when migration and convection effects are negligible is expressed by (Bockris and Reddy, 1970) using the Nernst equation.

\[
\eta_{\text{concentration}} = \frac{RT}{nF} \ln \frac{C_{x=0}}{C^o}
\]

(15)

where \(C_{x=0}\) is the concentration of the limiting reactant at the reaction site and \(C^o\) is the concentration of the limiting reactant in the bulk phase of the feed gas. The electronation or de-electronation current density is described using Fick's First Law of Diffusion.

\[
J_D = D \frac{dC}{dx}
\]

(16)

where the flux term \(J_D\) can be expressed as

\[
\frac{I}{nF} = J_D
\]

(17)

since the current density is proportional to the molar flux \((J_D)\). Equation (17) substituted into equation (16) gives the following if a linear concentration gradient is assumed,
\[ I = nFD \frac{(C^0 - C_{x=0})}{\delta} \]  
\( (18) \)

where \( \delta \) is the effective diffusion layer thickness. As the bias over the electrode is increased, the current density will increase and the concentration of the limiting reactant at the surface of the electrode will approach zero. When the concentration of the limiting reactant at the surface of the electrode reaches zero, the current density is at a maximum and is called the limiting current density as shown below.

\[ \frac{I_1}{nF} = J_D \]  
\( (19) \)

Substituting equation (19) and (18) into equation (15) and rearranging, the diffusion overpotential becomes

\[ \eta_{\text{concentration}} = \frac{RT}{nF} \ln \left( 1 - \frac{I}{I_1} \right) \]  
\( (20) \)

**Cathode Mathematical Model**

A mathematical model for correlating the cathode performance with scrubbed breathing air is considered here. If the reaction kinetics (activation-controlled current overpotential relationship) can be represented by the Butler-Volmer equation (12) an expression for mixed control
(activation and diffusion) can be represented by a modified Butler-Volmer equation [1].

\[ I = I_0 \left( \frac{C_{p,x=0}}{C_{p}^0} \exp \frac{\Delta F_n}{RT} - \frac{C_{Rx=0}}{C_{R}^0} \exp \frac{\Delta F_n}{RT} \right) \]  

\[ (21) \]

\( \frac{C_{i,x=0}}{C_{i}^0} \) is the ratio the limiting species' concentration at the electrode to its concentration in the bulk phase, where the subscript p represents the product and the subscript R represents the reactant. As shown earlier \( \frac{C_{i,x=0}}{C_{i}^0} \) is related to current.

The ratio \( \frac{C_{i,x=0}}{C_{i}^0} \) is determined by considering the zones of gaseous diffusion. In the first zone (flow cavity) the molar flux is described by the following equation,

\[ J_D = \frac{I}{nF} = -k g (C^0 - C^*) \]  

\[ (22) \]

where \( C^* \) is the concentration of oxygen at the entrance of the pore. \( C^0 \) is the concentration of oxygen in the bulk feed gas. In the second zone (the pore) the molar flux is represented by the following equation,

\[ J_D = \frac{I}{nF} = -D_{\text{eff}} \frac{(C^* - C_{x=0})}{\delta_g} \]  

\[ (23) \]

where \( C_{x=0} \) is the concentration of oxygen at the three phase reaction site. \( \delta_g \) is the diffusional boundary layer
thickness. The effective diffusivity is defined as follows:

\[ D_{\text{eff}} = D_{AB} \frac{\varepsilon}{\tau} \]  

(24)

where \( \tau \) is the tortuosity, \( \varepsilon \) the void fraction of the electrode, and \( D_{AB} \) the gaseous binary diffusivity. Since the flux in the cavity is equal to the flux in the pore, \( C^\circ \) can be eliminated when combining Equations (22) and (23) to give.

\[ \frac{C_{r,x=0}}{C_R} = 1 + \frac{I}{nFC^\circ} \left( \frac{1}{kg} + \frac{\tau\delta q}{D_{AB\varepsilon}} \right) \]  

(25)

The limiting current when \( C_{r,x=0} \) equals zero is

\[ I_L = -nFC^\circ \left( \frac{1}{kg} + \frac{\tau\delta q}{D_{AB\varepsilon}} \right) \]  

(26)

Equation (21) takes the Tafel form

\[ I = -I_0 (1 - \frac{I}{IL}) \exp \left( -\frac{\xi F n}{RT} \right) \]  

(27)

and the tortuosity (\( \tau \)), the exchange current density (\( I_0' \)) and the cathodic transfer coefficient (\( \alpha' \)) can be allowed to
be parameters which are varied to give the best fit to the data.

Mass transfer coefficients (kg) for laminar flow over a flat plate can be predicted with the following equations [45].

\[
(N_{sh})_L = \frac{k_G L}{D_{AB}} = 0.646 N_{Re,L}^{\frac{1}{2}} N_{Sc}^{1/3}
\]  

(28)

The length of the flow channel is taken to be 6.8 cm because of the irregular Exmet material, and the velocity of the gas is given by

\[
V = \frac{Q}{A_{CS}}
\]

(29)

where the cross sectional area \(A_{CS}\) of the flow channel is 1.9 cm. Binary diffusivities for gases can be predicted with the following equation [45].

\[
D_{AB} = 0.001 T^{7/4} \left( \frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2} \left[ \left( (V)^{1/3}_A + (V)^{1/3}_B \right)^2 \right]
\]

(30)

\(V\) is the atomic diffusion volume increments to be summed for each component, \(T\) is the temperature of the gas in degrees Kelvin, \(M\) the molecular weight, and \(P\) is the pressure of the gas in atmospheres. \(\delta g\) is taken to be the electrode thickness (0.034 cm) and \(\varepsilon\) is estimated at 0.5.
CONCLUSIONS

The concept of electrochemical gas concentration has been tested as a means for producing oxygen of sufficient quality for use as oxidant in alkaline fuel cells. A laboratory-scale cell was assembled using state-of-the-art components. Electrochemical design parameters were obtained with both breathing-air and propellant-oxygen feed. Purities of evolved oxygen exceeded the quality criterion for fuel-cell use. An economic analysis indicates the method is highly attractive as a means for on-site high-purity oxygen production.