

Fuel Composition Effects and Other Operational Parameters on Solid Oxide Fuel Cell Performance

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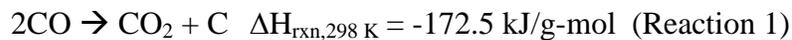
1. Introduction

This analysis will address the composition of coal derived synthesis gas (syngas), and the anticipated effect that the syngas chemical constituents have on the voltage of a solid oxide fuel cell (SOFC). All calculations and figures presented herein are done on a purely thermodynamic basis. This study does not account for limitations due to cell or stack design.

All simulations were conducted using an Aspen Plus 2004.1 model of an SOFC operating at atmospheric pressure. Unless otherwise noted, an SOFC overpotential of 118 mV was assumed. The Nernst potential was calculated based on exit temperature and composition, and the overpotential was subtracted to arrive at the cell operating voltage.

2. Effect of Water Concentration on Cell Voltage

It is assumed that at the anode inlet, an oxygen to carbon atomic ratio of greater than or equal to 2.0 ($O:C \geq 2.0$) is required to prevent carbon deposition from occurring via the Boudouard reaction:



To achieve this, steam is mixed with the syngas to achieve the appropriate ratio.

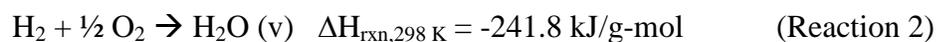
The effect that water vapor has on cell voltage becomes apparent by considering the voltage derivation. At low pressure, cell voltage can be approximated by using mole fractions:

$$V = \frac{-\Delta G}{2F} - \frac{RT * \ln K}{2F} \quad \text{Equation 1}$$

$$K = \frac{y_{H_2O}}{y_{H_2} * \left(\frac{y_{O_2}}{P}\right)^{\frac{1}{2}}} \quad \text{Equation 2}$$

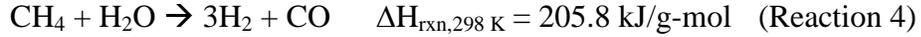
$$V = \frac{-\Delta G}{2F} - \frac{RT}{2F} \ln \left[\frac{y_{H_2O}}{y_{H_2} * (y_{O_2} * P)^{\frac{1}{2}}} \right] \quad \text{Equation 3}$$

This derivation assumes that the hydrogen oxidation reaction is solely responsible for cell voltage:



Gibbs energy change for this reaction is negative, therefore the first term on the right hand side of Equation 3 is a net positive number. As a result, voltage decreases as water concentration increases.

Other reactions that affect the water concentration in the SOFC include the water gas shift reaction (Reaction 3), and the methanation reaction (Reaction 4):



The SOFC model used in this analysis considers all three reactions (Reactions 2–4), with the final state of the system determined by thermodynamic equilibrium.

2.1. Low Methane Syngas Case

Figure 1 demonstrates the effect that water concentration of a low methane content syngas has on voltage. The syngas composition that was assumed, which is typical of a two-stage, slagging, full slurry quench gasifier such as ConocoPhillips' E-Gas, is shown in Table 1.

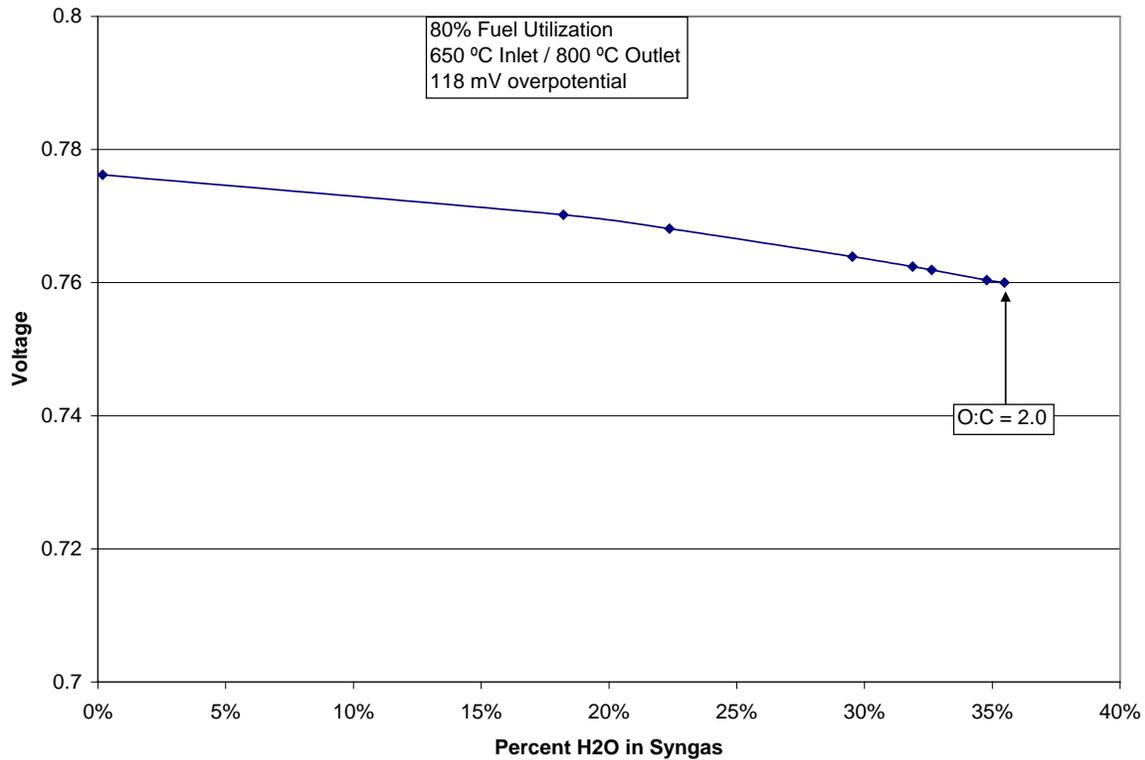
Table 1 – Low Methane Syngas Composition¹

N ₂ (mol fraction)	1.2%
Ar	0.9%
H ₂	32.4%
CO	45.5%
CO ₂	15.1%
H ₂ O	0.2%
CH ₄	4.7%

To generate the data in Figure 1, water was added until the O:C ≥ 2.0 criteria was satisfied, which was at approximately 36% H₂O. This point represents realistic anode feed conditions with respect to water concentration, to avoid carbon deposition. At 36% H₂O in the SOFC feed, the cell voltage reduction was approximately 3% compared to the dry feed case.

¹ The syngas composition is assumed to be after a dry gas cleaning system, where there would be no moisture present.

Figure 1 - Effect of Water Concentration on Cell Voltage for Low Methane Syngas



2.2. High Methane Syngas Case

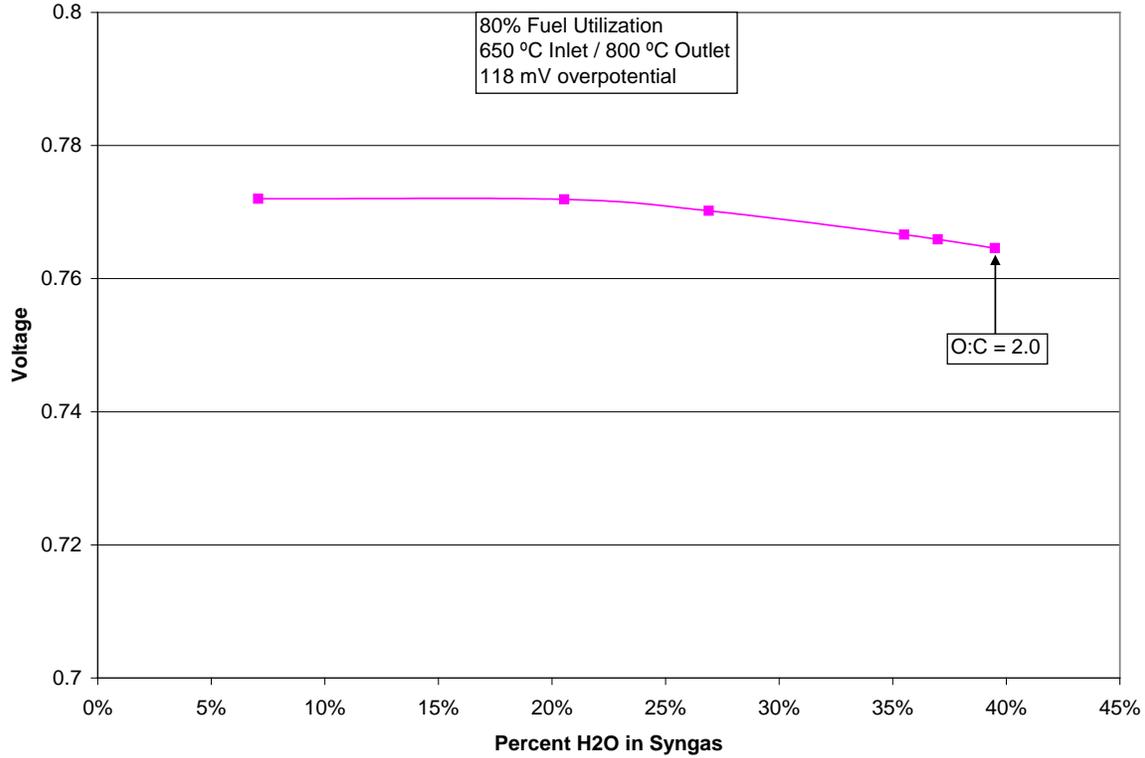
A high methane syngas was also considered, to determine the effect of water concentration on cell voltage. The syngas composition assumed would be representative of an advanced catalytic coal gasifier following a cold gas cleaning system (such as the Selexol process), and is shown in Table 2.

Table 2 - High Methane Syngas Composition

N ₂ (mol fraction)	1.0%
H ₂	26.0%
CO	8.0%
CO ₂	36.0%
H ₂ O	0%
CH ₄	29.0%

Figure 2 demonstrates the effect that water concentration has on cell voltage for high methane syngas. To generate the data in Figure 2, water was added until the $O:C \geq 2.0$ criteria was satisfied, which was at approximately 40% H₂O. This point represents realistic anode feed conditions with respect to water concentration, to avoid carbon deposition. At 40% H₂O in the SOFC feed, the voltage reduction is minimal compared to the dry feed case (1% reduction).

Figure 2 - Effect of High Methane Syngas Water Concentration on Voltage



It is assumed that methane will combine with steam within the SOFC to produce hydrogen (as opposed to direct anode oxidation) according to the endothermic methane reforming reaction (Reaction 4, $\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}$). This reaction consumes one mol of H_2O per mol of methane consumed, and also produces CO , which further consumes H_2O via the water gas shift reaction (Reaction 3, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$).

When high methane syngas is the fuel, water is consumed by two separate mechanisms (methane reforming and water gas shift). With low methane syngas, H_2O is consumed only by the water gas shift reaction. Therefore, the presence of water vapor has even less of an effect on cell voltage when the fuel is high in methane, compared to low methane fuel.

3. Effect of Fuel Utilization on Cell Voltage

As hydrogen fuel is consumed in the fuel cell, its concentration in the syngas falls, and water is produced, increasing the H_2O concentration in the product gas. The logarithmic term in Equation 3

$$V = -\frac{\Delta G}{2G} - \frac{RT}{2F} \ln \left[\frac{y_{\text{H}_2\text{O}}}{y_{\text{H}_2} (y_{\text{O}_2} * P)^{\frac{1}{2}}} \right]$$

relates the concentration of water and hydrogen to the cell voltage. For high fuel utilization, the concentration of water will be at a maximum, and the concentration of hydrogen a minimum. This will cause the logarithmic term in Equation 3 to be large, resulting in a decrease in cell voltage.

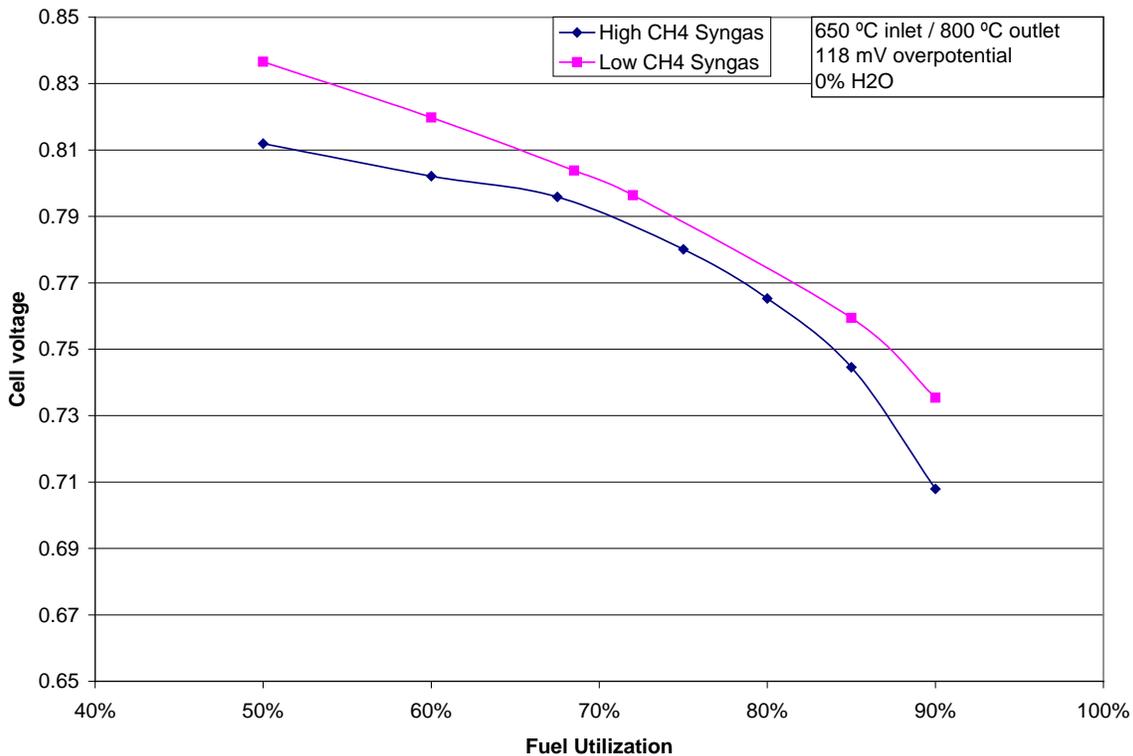
Stated another way, if only the hydrogen term in Equation 3 is considered, and denoting that the hydrogen partial pressure changes from P_1 to P_2 , the resulting voltage change is:

$$\Delta V = \frac{RT}{2F} \ln\left(\frac{P_2}{P_1}\right)$$

The partial pressure of hydrogen is constantly decreasing as it is consumed, therefore P_2 is always less than P_1 , and the logarithmic term above will be a negative number. Therefore, the change in voltage is always negative as fuel utilization increases. As more hydrogen is consumed (higher fuel utilization), the change in voltage increases in magnitude.

Figure 3 shows the effects of fuel utilization on cell voltage for both high and low methane syngas (Table 2 and Table 1, respectively). For all cases, the cell voltage of the low methane syngas was slightly higher than for high methane fuel. It should be noted that the voltages in Figure 3 are for fuels that have no water vapor present. The combined effect of water vapor and fuel utilization will be explored further in the next section.

Figure 3 - Effect of Fuel Utilization on Cell Voltage



4. Effect of Water Concentration and Fuel Utilization on Cell Voltage

Section 2 and Section 3 showed the individual effects of water content and fuel utilization on cell voltage. Syngas water vapor concentration was shown to have a minimal impact on voltage, while the effect of fuel utilization was somewhat greater. This section will address the combined effects of both water concentration and fuel utilization on cell voltage.

Figure 4 illustrates the impact of these two variables for low methane content syngas (see Table 1) for three fuel utilizations: 50%, 65%, and 80%. The point at approximately 35% H₂O content represents an O:C ratio of 2.0, and is the concentration that would be typical of anode feed in an integrated gasification fuel cell (IGFC) combined cycle.

Figure 5 illustrates the impact of these two variables for high methane content syngas (see Table 2) for three fuel utilizations: 50%, 65%, and 80%. The point at approximately 40% H₂O content represents an O:C ratio of 2.0, and is the concentration that would be typical of anode feed in an integrated gasification fuel cell (IGFC) combined cycle.

Figure 4 – Combined Effect of U_f and H₂O Content on Cell Voltage for Low CH₄ Syngas

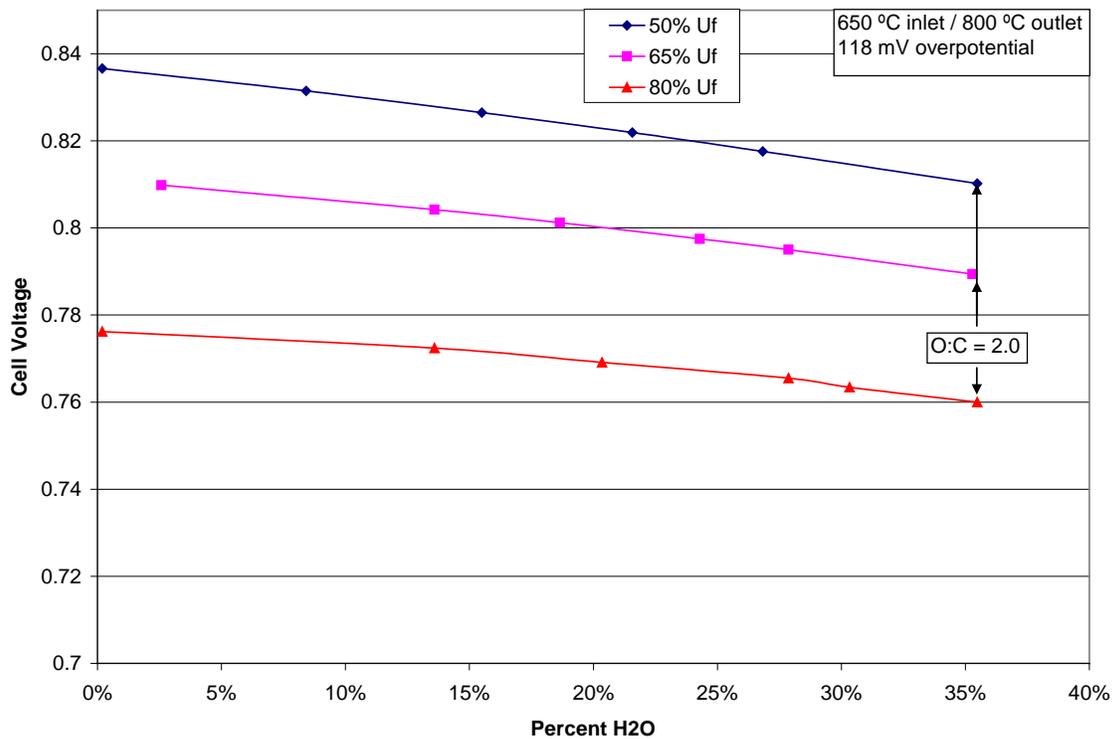
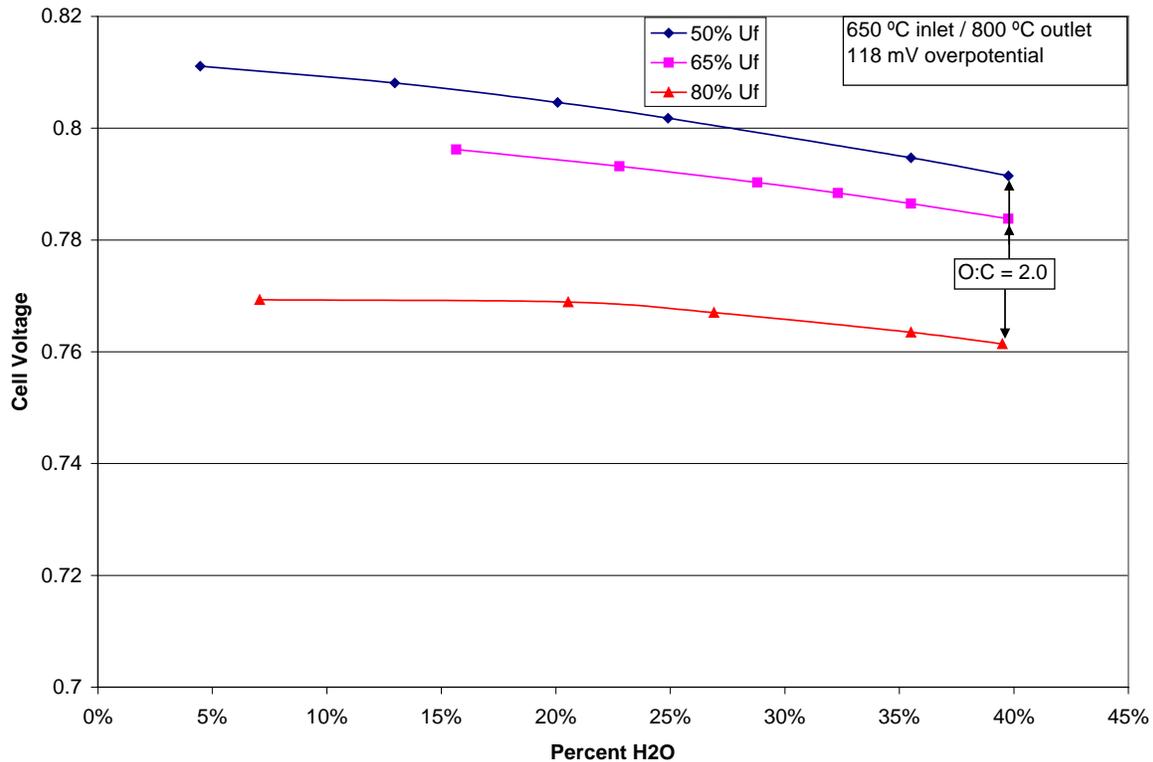


Figure 5 - Combined Effect of U_f and H_2O Content on Cell Voltage for High CH_4 Syngas



5. Effect of Anode Recycle on Cell Voltage

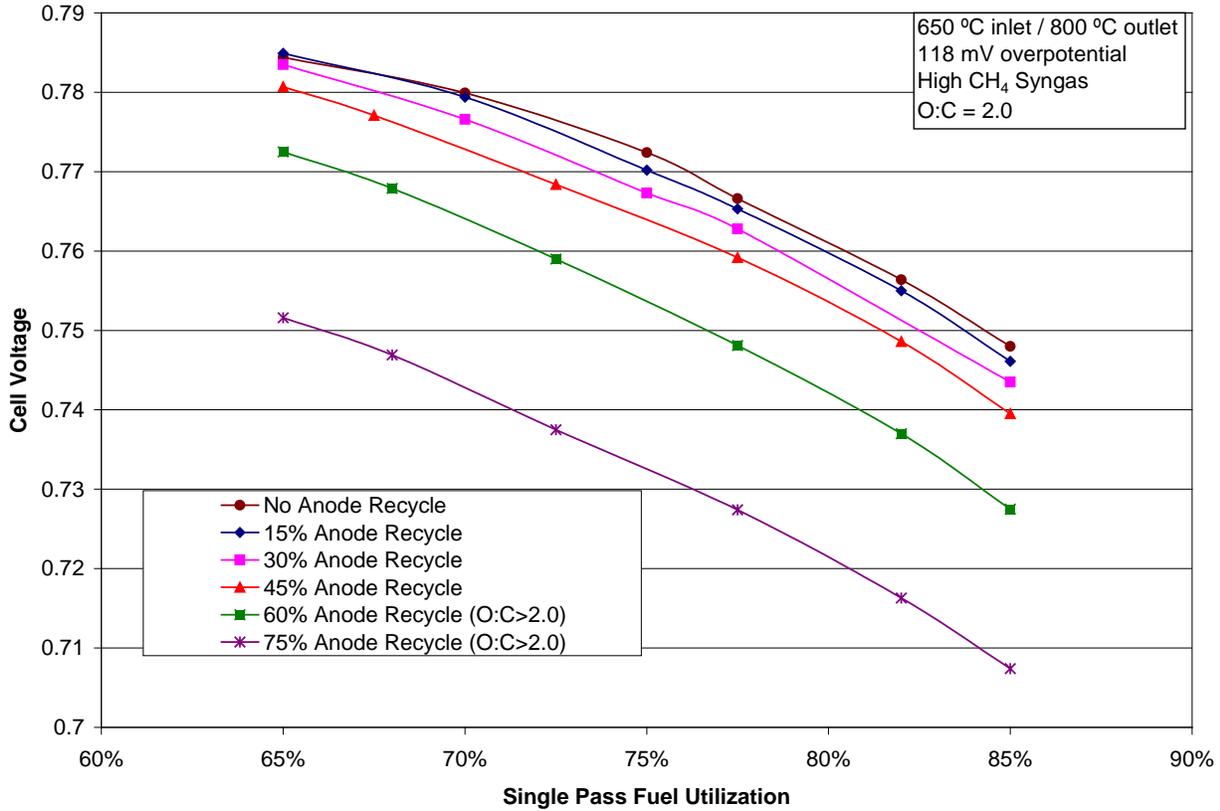
This section will address the effect of anode recycle on cell voltage. By recycling a portion of the anode effluent back through the fuel cell, the single pass fuel utilization can remain low, while the overall utilization is higher. The degree of the overall fuel utilization is set by the anode recycle rate.

Figure 6 shows the effect of anode recycle (0-75% recycle) on cell voltage over a range of single pass fuel utilizations (65-85%). For a given single pass utilization, cell voltage decreases as anode recycle increases. This is due primarily to the increased amount of inerts (H_2O and CO_2) at the anode inlet caused by recycle.

As discussed previously increased water content decreases the cell voltage slightly according to Equation 3. The elevated CO_2 concentration also assists in keeping water concentration high by thermodynamically limiting the water gas shift reaction (Reaction 3).

All curves in Figure 6 had supplemental steam mixed with syngas at the anode inlet, in order to achieve an oxygen-to-carbon atomic ratio of 2:1 (to prevent carbon deposition via Reaction 1). For the cases with high recycle rates (60 and 75% anode recycle), there was no need for supplemental steam because the O:C ratio at the anode inlet was already greater than 2.0, due to high concentrations of recycled water and CO_2 . These additional diluents served to lower voltage by inhibiting the hydrogen oxidation (Reaction 2) and water gas shift reactions (Reaction 3).

Figure 6 - Effect of Anode Recycle on Cell Voltage



6. Conclusions

This analysis shows that for both high and low methane syngas, water concentration has a minimal effect on cell voltage. The effect on low methane syngas was slightly greater than the effect on high methane syngas.

The effect of fuel utilization on cell voltage for a dry syngas was approximately the same for both the high and low methane cases. Over a range of 50 – 90% single pass fuel utilization, cell voltage decreased approximately 12%. When adequate moisture was added to the syngas to achieve a 2.0 O:C ratio, the combined effect of water and fuel utilization on cell voltage did not change appreciably (compared to the dry syngas case).

Anode recycle is an effective method to achieve high overall fuel utilization, however it does introduce high levels of diluents (both H₂O and CO₂) into the anode inlet gas. While H₂O alone had almost a negligible effect on cell voltage, the combined effect of H₂O and CO₂ was slightly greater. This is presumably due to the presence of CO₂, which keeps water concentration high by thermodynamically limiting the water gas shift reaction. Even so, for low recycle rates (0-45%), this had an effect of one percent or less on cell voltage. It should

be noted that industry teams are currently focused on anode recycle rates of approximately 45-50%, and cell voltage is therefore not expected to be impacted significantly.

For higher anode recycle rates (60 – 75%, and above), the diluent levels are so high (O:C >> 2.0) that voltage starts to become somewhat more inhibited according to the logarithmic term in Equation 3:

$$V = -\frac{\Delta G}{2G} - \frac{RT}{2F} \ln \left[\frac{y_{H_2O}}{y_{H_2} (y_{O_2} * P)^{\frac{1}{2}}} \right]$$

At 60% anode recycle, there was a cell voltage decrease of approximately 1.5 - 2.5% compared to the no recycle case (see Figure 6). For 75% anode recycle, the cell voltage decrease ranged from approximately 4.5 - 5.5% compared to the no recycle case.