Flow and reaction in a tubular solid oxide fuel cell

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A solid oxide fuel cell (SOFC) is a device that can produce electricity directly from the combustion of a fuel. Zirconia, a ceramic solid, has the property that it can conduct oxygen ions at high temperatures, typically between $700^{\circ}C$ and $1000^{\circ}C$. When fuel is reacted on one side of a piece of heated zirconia, a deficiency in oxygen is created. If the other side is exposed to atmospheric oxygen and isolated from the other side, we have an oxygen concentration gradient across the zirconia, with high concentration on the air side and low concentration on the fuel side. By using electrodes on each side of the zirconia we can create a circuit which is completed by the flow of oxygen ions across the zirconia. Molecular oxygen and electrons combine at the cathode to form negatively charged oxygen ions. These ions then flow across the zirconia electrolyte to the anode where they are converted back into molecular oxygen, which is burnt with the fuel, and electrons, which are carried by the circuit.

The oxygen reacts with hydrogen on the surface of the anode via reaction (3) so that the fuel cell is essentially running on hydrogen, and there is a waste product, water. However, because hydrogen is not a primary fuel, we need to produce it from other hydrocarbons. We reform methane (CH_4) using steam via reaction (5), and this is accompanied by the water gas shift reaction (6). The carbon monoxide produced in these two reactions can also react with the oxygen via reaction (4). The complete reaction scheme is

Cathode:
$$2O_2 + 8e^- \rightarrow 4O^{2-}$$
 (1)

- Anode: $4O^{2-} \to 2O_2 + 8e^-$ (2)
 - $2H_2 + O_2 \rightleftharpoons 2H_2O \tag{3}$
 - $2CO + O_2 \rightleftharpoons 2CO_2 \tag{4}$
- $CH_4 + H_2 O \rightleftharpoons CO + 3H_2 \tag{5}$
 - $CO + H_2 O \rightleftharpoons CO_2 + H_2$ (6)



Figure 1: Diagram of the tubular SOFC, with the co-ordinate system.

The cell, illustrated in figure 1, is approximately 20cm long and has internal radius 0.9mm, whilst the electrode is approximately 1.3cm long. The electrolyte layer thickness is about 10^{-6} m. The aspect ratio of the cell is small, and we define $\epsilon = \frac{a}{b} \ll 1$.

A mixture of methane and water is preheated to the cell temperature, and fed into one end of the tube, with a typical flowrate of 25 ml min⁻¹. The chemical reactions take place on the surface of the

anode, in the presence of a nickel catalyst. We find that the effects of upstream diffusion are so small that the mixture is unchanged until it reaches the region of the electrodes. Here the electrochemistry and surface reactions take effect.

Since an oxygen molecule produces 2 oxygen ions, each carrying 2 electrons,

$$i(z) = 4Fq_e(z),$$

where i(z) is the current density at position z along the axis of the tube, $q_e(z)$ is the oxygen flux density and F is Faraday's constant.

Nernst's equation for the local voltage E(z), is

$$E(z) = \frac{RT}{4F} \ln\left(\frac{\rho_a Y_{oa}}{\rho Y_o}\right),$$

where R is the gas constant, T the cell temperature, which experimental measurements show to be almost constant, ρ the mixture density and Y_{oa} the mass fraction of oxygen in the atmosphere, with Y_o the local value of the mass fraction of oxygen inside the cell. This equation tells us that the voltage depends only on the amount of oxygen on the fuel side of the cell.

These equations can be combined to give an expression for q_e in terms of the oxygen mass fraction and the mixture density as

$$q_e = \frac{RT}{16F^2R_s} \left(\ln\left(\frac{\rho_a Y_{oa}}{\rho Y_o}\right) - \frac{4F}{RT} E_{cell} \right) \left(H(z-z_1) - H(z-z_2) \right),$$

where R_s is the specific resistance of the electrolyte and the electrodes and E_{cell} is the cell potential. In addition, the total current I produced by the cell is found to be

$$I = 8\pi a F \int_{z_1}^{z_2} q_e(z) dz.$$

Note that because the electrochemistry only takes place under the electrodes, we have used the composite Heaviside function $(H(z - z_1) - H(z - z_2))$ so that $q_e = 0$ outside this region.

We will seek solutions for the mass fractions Y_i for each of the six different chemical species involved in the reactions, where the subscript *i* can represent *f* (*fuel-methane*), *w*(*water*), *o*(*oxygen*), *h*(*hydrogen*), *m*(*carbon monoxide*) and *d*(*carbon dioxide*). In particular the solution for Y_o will enable us to predict the current for specified values of the voltage.

We use conservation of linear momentum in the lubrication limit $\epsilon \ll 1$ to find the radial and axial components v_r and v_z of the mixture velocity. These can be found in closed form and used in the mass conservation equation for each species to give the dimensionless, axisymmetric equations for an idealised infinitely long fuel cell in which the anode lies in the region $0 \le z \le 1$, which we solve for each Y_i in the domain $-\infty < z < \infty$, $0 \le r \le 1$,

$$-\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial Y_i}{\partial r}\right) + \frac{1}{2}Q_0\epsilon\left(\left(r^2 - 1\right)\frac{\partial}{\partial z}\left(\frac{\rho Y_i}{M_1}\right) - \frac{1}{r}\frac{\partial}{\partial r}\left(Y_i\frac{\partial}{\partial z}\left(\frac{M_r}{M_1}\right)\right)\right)$$
$$+\epsilon^2\left(E_0\left(\left(r^2 - 1\right)\frac{\partial}{\partial z}\left(\frac{\rho Y_i}{M_1}\int_0^z q_e\left(s\right)ds\right) - \frac{1}{r}\frac{\partial}{\partial r}\left(Y_i\frac{\partial}{\partial z}\left(\frac{M_r}{M_1}\int_0^z q_e\left(s\right)ds\right)\right)\right) - \frac{\partial^2 Y_i}{\partial z^2}\right) = 0.$$

In these equations the integral M_R is defined as

$$M_R = \int_0^R (s^3 - s)\rho(s, z)ds.$$

Note that here we have defined two dimensionless parameters, $E = \frac{am_oRT}{16F^2R_s\rho_{in}D}$, where m_o is the molecular mass of oxygen and D is the gas diffusivity, and $Q = \frac{Q_{in}}{\pi h \rho_{in}D}$, where Q_{in} is the upstream flowrate of the mixture. We have used experimental data to establish that $E = E_0 \epsilon^2$ and $Q = Q_0 \epsilon$, (where E_0 and Q_0 are O(1) quantities) in deriving these equations.

We also have the boundary conditions which contain all the information about the reactions on the anode surface. In the case of the methane fraction Y_f ,

$$\delta \left[\frac{\partial Y_f}{\partial r} + Y_f E_0 q_e \right] = \left(H(z) - H(z-1) \right) \epsilon^2 \left[\frac{-\rho^2 Y_w Y_f}{m_w} \right] \text{ at } r = 1.$$

 m_w is the molecular mass of water. There are similar conditions for the other mass fractions. We define a second small parameter $\delta = \frac{aDm_f}{k_1h^2\rho_{in}}$, where k_1 is the reaction rate constant associated with the steam reforming reaction (5) and ρ_{in} is the density of the input mixture. This parameter reflects the dominance of the reaction process over diffusion in the cell.

Away from the electrode region, where electrochemistry and reaction do not occur, these boundary conditions simplify to $\frac{\partial Y_i}{\partial r} = 0$ at r = 1. In addition we have the symmetry condition $\frac{\partial Y_i}{\partial r} = 0$ at r = 0, and the input conditions $Y_f = Y_{f(in)}, Y_w = Y_{w(in)}$, and $Y_i = 0$ for the other species as $z \to -\infty$, where these values represent the composition of the input mixture. Far downstream of the electrode we have a uniform mixture of reaction products which we seek to determine.

In order to solve these equations we express each mass fraction Y_i as a perturbation series as follows,

$$Y_i = Y_{i0} + \epsilon Y_{i1} + \epsilon^2 Y_{i2} + \ldots + \epsilon^\mu Y_{i\mu} + \frac{\delta}{\epsilon^2} \bar{Y}_{i0} + \frac{\delta}{\epsilon} \bar{Y}_{i1} + \delta \bar{Y}_{i2} + O(\delta\epsilon)$$

and we can solve the equations for Y_i in various asymptotic regions as shown in figure 2.

Upstream of	Anode front	Anode region, 0 <z<1< th=""><th>Anode back</th><th>Downstream of</th></z<1<>	Anode back	Downstream of
anode, z<0	boundary layer	· • •	boundary layer	anode, z>1
	width O(ɛ)		width O(ɛ)	
		· · · · · · · · · · · · · · · · · · ·		:
$\mathbf{Y}_{\mathrm{f}} = \mathbf{Y}_{\mathrm{f(in)}}$	$Y_{\rm f} = O(1)$	$Y_f = O(1)$	$Y_{\rm f} = O(1)$	$Y_{\rm f} = O(1)$
$\mathbf{Y}_{w}=\!\mathbf{Y}_{\!w(in)}$	$Y_w = O(1)$	Y _w =O(δ)	$Y_w = O(\delta)$	$Y_{w} = O(\delta)$
else $Y_i = exp.small$	$Y_h = O(1)$	$Y_h = O(1)$	Y _h =O(1)	Y _h =O(1)
ρ =O(1)	$Y_m = O(1)$	Y _m =O(1)	Y _m =O(1)	Y _m =O(1)
	$Y_{o} = O(\delta)$	Υ ₀ =Ο(δ)	$Y_{o} = O(\delta)$	$Y_{o} = O(\delta)$
	$Y_d = O(\delta)$	$Y_{d} = O(\delta)$	$Y_{d} = O(\delta)$	$Y_{d} = O(\delta)$
_	ρ =O(1)	ρ =O(1)	ρ =O(1)	ρ =O(1)
	z=0		z=1	
anode				
	<		>	

Figure 2: Asymptotic structure of the solution.

From our solutions we are able to obtain information about the current-voltage variation of the device, and make predictions for various inflow conditions.