Fundamental Considerations of Fuel Cells for Mobility Applications

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Future Engines and Their Fuels
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Motivation

• Reducing the fuel consumptions of our mobility systems is of paramount importance

• Necessitates a fundamental evaluation of what are the practical limits of efficiency for our mobility systems
  – This has been an active area within the ERC with a focus on IC Engines

• Need to supply a similar, fundamental analysis of practical limits to other candidate power plants and fuels
  – Fuels Cells
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Maximum Theoretical Work from a Thermodynamic Process

\[ W_{\text{max}} = -\Delta G \]

- IC Engines and Fuel Cells are similar energy converters
  - Both convert the “chemical” internal energy in the fuel into work and exhaust the spent fuel and oxidizer (products)
- Both are governed by the same thermodynamic relationship for maximum theoretical work
  - Both are chemical engines in which the energy transformation is accomplished via a chemical reaction in a thermodynamic process
Differences Between IC Engines and Fuel Cells

- **IC Engine**
  - The energy conversion of the fuel is accomplished via a chemical reaction
  - The charge transfer occurs directly between two chemical species without the liberation of free electrons

- **Fuel Cell**
  - The energy conversion of the fuel is accomplished via an electrochemical reaction
  - The charge transfer of the reaction is physically separated and takes place between electrodes and the respective chemical species
Implications of this on the Thermodynamic Analysis

• **IC Engine**

\[ W_{\text{max}} = -\Delta G_{\text{rxn}} \]

\[ W_{\text{max}} = -(H_{\text{prod}} - H_{\text{react}}) + T_0(S_{\text{prod}} - S_{\text{react}}) = Q_{HV} + T_0(S_{\text{prod}} - S_{\text{react}}) \]

• **Fuel Cell**

\[ W_{\text{elect}} = nFE = -\Delta G_{\text{rxn}} \]

where: \( n \) = number of moles of electrons

\( F \) = Faraday's constant

\( E \) = potential difference
Simple Fuel Cell Example

At standard temperature and pressure consider:

\[ H_2 + \frac{1}{2} O_2 \rightleftharpoons H_2O \]

\[ \Delta G := -237 \cdot 10^3 \frac{J}{\text{mole}} \quad \text{n} := 2 \quad \text{Faraday} := \left(96485.3383 \frac{\text{coul}}{\text{mole}}\right) \]

\[ E := \frac{-\Delta G}{n \cdot \text{Faraday}} \quad \text{E} = 1.228 \text{volt} \]

To obtain higher voltages one uses a stack of many individual cells.
Further Development of the Fuel Cell
Maximum Work Expression

• Nernst Equation

\[ W_{\text{elect}} = nF \varepsilon = - \Delta G_{\text{rxn}} \]

\[ E = - \frac{\Delta G_{\text{rxn}}}{nF} \]

realize: \( E = f(T, P, \mu_i) \)

with: \( \mu_i = \mu_0(P_o, T) + RT \ln a_i \)

where: \( a_i = \text{activity} = \frac{f_i}{f_i^o} = \frac{P_i}{P_o} \) (ideal gas)

\[ E = E^o - \frac{RT}{nF} \ln \frac{\Pi a_i^{\nu_i}_{\text{products}}}{\Pi a_i^{\nu_i}_{\text{reactants}}} \]

\( E^o \) = Standard state reversible voltage
Electrochemistry Includes Movement in a Potential Field

\[ \tilde{\mu} = \mu_i + z_i F \phi_i = \mu_i^0 + RT \ln a_i + z_i F \phi_i \]

with: \( z_i \) = charge number, \( F \) = Faraday's constant, \( \phi_i \) = electrical potential experiences by species \( i \)

- Now we must also consider electrical potential with the chemical potential – electrochemical potential
- There is a change in the electrochemical potential experienced by the electrons as they move from the anode to the cathode (a source of entropy generation)
Practical Fuel Cell Efficiency

• Need to account for:
  – Voltage losses
    • Chemical activation losses
    • Ohmic losses
    • Mass transport – diffusive (concentration) losses
  – Fuel Utilization losses
    • Accounting for the fact that not all of the fuel provided to the fuel cell participates in the electrochemical reaction

• This performance is given in current-voltage curves
Current – Voltage Curve

Electrochemical Processes are Heterogeneous

Steps in an Electrochemical Reaction:

1. Mass transport to the electrode
2. Absorption of the $\text{H}_2$ onto the electrode surface
3. Separation of $\text{H}_2$ into two chemisorbed $\text{H}$ atoms on electrode surface
4. Transfer of electrons of chemisorbed $\text{H}$ atoms to electrode – releasing $\text{H}^+$
5. Mass transport of $\text{H}^+$ away from the electrode

Schematic of Electrochemical Process

Chemical Activation Losses

- Electrochemical reactions take place at an interface between the electrode and electrolyte.
- Current density is a more fundamental metric than current – which then causes a focus on per-unit-area reaction rates.
- Reaction rate is determined by the activation energy (barrier).
- In electrochemical reactions the activation energy can be manipulated by varying the cell potential:
  - The free energy of a charged species is sensitive to voltage – changing the voltage of the cell changes the size of the activation barrier.
- The current produced with a fuel cell increases exponentially with activation overvoltage (voltage which is sacrificed to overcome the activation barrier).
  - We sacrifice part of the thermodynamically available cell voltage to produce a net current.
- Activation overvoltage occurs at both the anode and cathode.
Schematic of Activation Losses

Activation losses from H$_2$ – O$_2$ fuel cell anode versus cathode


Relationship between the current density output and the activation overvoltage is exponential and is know as the Bulter – Volmer equation.
Minimizing Activation Overvoltage Losses

1. Increase reactant concentration
   - Has an impact on cell voltage – Nernst Eq.
2. Increase reaction temperature
   - Nernst Eq. - this slightly reduces voltage
3. Decrease activation barrier – catalyst
4. Increase the number of reaction sites (high surface area electrodes)
Ohmic Losses (Charge Transport)

- Accumulation/depletion of electrons at the two electrodes creates a voltage gradient which drives the transport of the electrons.

- In the electrolyte the accumulation/depletion of protons creates both a voltage gradient and a concentration gradient which drives the transport of the protons from the anode to the cathode.

Charge Flux = $\sigma \frac{dV}{dx}$; $\sigma$ = conductivity, $V$ = voltage

Ohmic Losses

- Charge transport contributes to a linear decrease in operating voltage
- Ionic charge transport tends to be more difficult than electronic charge transport – ionic transport resistance dominates
- Fuel cell resistance scales with electrolyte thickness
- Resistances within the fuel cell are additive

\[ \eta_{\text{ohmic}} = iR_{\text{ohmic}} = i(R_{\text{elect}} + R_{\text{ionic}}) \]

Ohmic Losses Summary

• Voltage that is expended to drive conductive charge transport is a loss
  – Ohms law
• Resistance is dominated by ionic charge transport
  – Thickness is an important parameter
• Electrolyte choice is very important
  – Liquid
  – Polymer
  – Ceramic
Mass Transport

- Mass transport governs supply and removal of reactants and products
- Mass transport to the fuel cell electrodes is typically dominated by diffusion
  - Diffusive transport limitations in the electrode lead to a limiting current density (reactant concentration falls to zero at the fuel cell catalyst layer)
  - Reactant depletion affects both the Nernstian cell voltage and the kinetic reaction rate
- Mass transport in fuel cell flow structures is typically dominated by convection
  - Viscosity and pressure drop (design) impact these losses

Mass Transport Couples with the Nernst Equation

- Electrochemical reaction drives diffusion by reducing the concentration of the reactant at the electrode surface
  - Concentration depletion at the surface reduces the voltage – Nernst Eq
  - Reactant concentration at the catalyst surface decreases, and product concentration at the catalyst surface increases, relative to bulk concentration – increases activation losses (not included in the figure)

Summary of Thermodynamic Losses in a Fuel Cell

\[ V = E_{\text{thermo}} - \eta_{\text{act}} - \eta_{\text{ohmic}} - \eta_{\text{conc}} \]
Performance Summary

- The performance curve given for a particular fuel cell is the result of unavoidable losses

Efficiency at Peak Power

• Efficiency at peak power ~ 48%
• Does not include conversion of electricity to rotational motion
Closing Comments

Fuel Cell Thermodynamic Challenges
• Raising the efficiency at high load
• Issues to be addressed:
  – Voltage losses - (thermodynamically associated with power generation), Ohmic losses, and Diffusive losses
• High load efficiency is inferior to IC Engine

IC Engine Thermodynamic Challenges
• Raising efficiency at low load
• Issues to be addressed
  – Pumping work, Combustion gas γ control (temperature and composition), exhaust energy
• Low load efficiency is inferior to Fuel Cell
  – Hybridization, etc

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Social or External Constraints

• Cost
• Perceived Utility (mobility paradigm):
  – Range, performance, availability of an acceptable energy carrier, local emission signature, noise, convenience of use…..
• Life cycle ecological footprint
• Etc. (how easily they connect with iCloud).
Thank you very much

http://www.erc.wisc.edu/