Research on Hydrogen and Fuel Cells

This article is based on a lecture delivered at ICT as an activity of Indian Institute of Chemical Engineers, Mumbai Regional Centre.
The material of the lecture has been compiled by the Bombay Technologist Editorial Team.

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1. Introduction

The world is facing a major energy crisis; the reasons being, over 85% of the energy consumed is being obtained from fossil fuels. United States of America consumes about 25% of the world's energy. With the diminishing fossil fuels and oil, the world's energy need in the 21st century can only be met with the utilization of the non-conventional energy resources like solar energy, wind energy, geothermal energy, nuclear energy, carbon etc.

2. Green House Effect

Green house effect is mainly caused due to usage of fossil fuels. Global warming is a greater concern than the depletion of Earth's reserves of fossil fuels. There has already been a rise of 0.6°C in global temperatures on account of industrialization as compared to the 'pre-industrialization' era. At this rate, the projected rise is temperature is about 3°C in the future. Small temperature variations can cause catastrophic differences in climate. Some of the disastrous effects of the Green House effect are marine environment changes, hurricane intensification, climate alteration, desertification, glaciers melting.

To avert such occurrences, societies need to rethink their fuel strategy.

Energy security has become an issue under the shadow of global warming and the need to reduced greenhouse gas emissions is increasing by 1.5% every year. H_2 is now being looked at as a fuel.

3. Hydrogen Economy

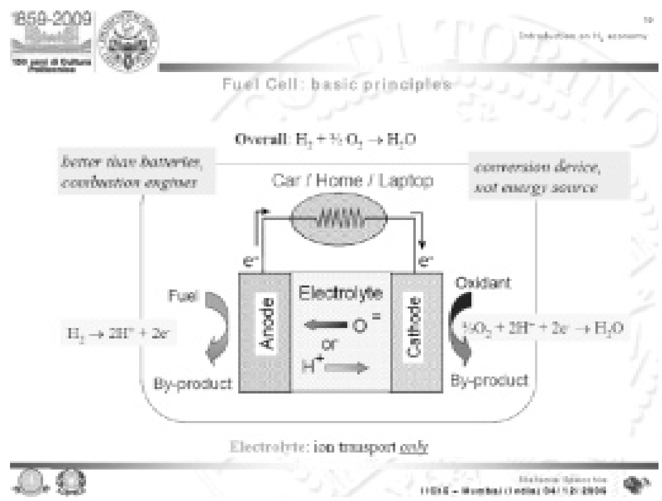
The hydrogen economy describes a system in which our energy needs are predominantly met by hydrogen, rather than fossil fuels. This type of economy would rely on renewable resources in the form of hydrogen gas and water, drastically changing pollution, electricity sources, infrastructure, engines, and international trade, without impacting our quality of life. In a hydrogen economy, vehicles like cars and airplanes use hydrogen fuel cells for power, rather than petroleum distillates.

By conceiving of a hydrogen economy, we are referencing our increasing demand for clean-burning fuels that do not cause air and water pollution nor make us dependent on dwindling energy sources. It's important to see the ideal of the hydrogen economies simultaneously addressing several problems with the current state of petroleum reliance. It is motivated by a combination of economics and environmentalism.

Hydrogen is the most attractive fuel for fuel cells which can be an important source of energy for the future.

4. Hydrogen Fuel Cell

The basic principles of the H_2 fuel cell can be explained with the help of the following diagram.



Connecting many cells, with every single cell comprising of bipolar plates, anode, cathode and electrolyte stacks, it is possible to obtain the desired power.

H_2 is the most attractive fuel for Fuel Cell applications. This is due to the following properties-

1. Excellent Electrochemical Activity
2. Adequate Levels of Power Density in an H_2/ Air System for Vehicles Propulsion
3. Zero Emission Characteristics

However currently there are certain major difficulties in adoption of the Hydrogen economy. A steady and continuous supply of hydrogen is itself an issue. This is because H_2 must be manufactured from either fuels or water before it can be used as a fuel. Thus we once again have to resort the use of our depleting and also polluting resources such as the fossil fuels. Storage and handling of hydrogen is also cumbersome. Very large containers are required for storage of even small amounts of the gas.

Today, approximately 95% of all H_2 produced is by STR steam reforming of Natural gas, the most energy efficient large scale method with CO_2 as a by-product. H_2 fuel cells are a green solution paving way for reduced emissions, as they have a high electrical efficiency of about 40-60%.

5. H_2 as an Automotive Fuel

The efficiency of H_2 as an automotive fuel, as an alternative to liquid fuel is being considered.

Fuel cell power systems are durable and reliant as current automotive engines.

They have a 5000 hour or a 1.5×10^5 miles equivalent lifespan. They are able to function over the full range of environmental conditions, from -40°C to +40°C.

The factors affecting the durability of these fuel cells are catalyst layer degradation,gas diffusion layer degradation, carbon support corrosion,degradation of the polymeric membrane.

6. Difficulties Involved in H_2 Fuel Economy

Despite all the benefits associated with H_2 fuel economy, several barriers still stand in the path of its implementation. Lack of infrastructure for the generation and distribution of H_2 in appreciable quantities, lack of storage systems not completely reliable fuel processor technology, CO clean up (< 10 ppmv; 50ppmv as a peak), dynamic states management and emissions during cold start up.

Water management must be undertaken as it protects mainly at cold winter time, and water consumptions balance between FC stack and fuel processor (FP) Weight and volume required for the fuel. Present costs are at 15,000$ / kW and the goal is 50$ / kW for the whole system

7. Established Routes to H_2 Production

The different routes of hydrogen production have been mentioned below.

1. Nuclear Energy → water Thermolysis → H_2
   Nuclear Energy → thermoelectric cycles → water Electrolysis → H_2
2. Biomass waste → Gasification → synthesis gas → H_2
   Biomass waste → Metabolism → H_2
   Biomass waste → Fermentation → Biogas reforming → synthesis gas → H_2
   Biomass waste → thermoelectric cycles → water Electrolysis → H_2
3. Geothermal → thermoelectric cycles → water electrolysis → H_2
4. Solar Energy → thermoelectric cycles → water electrolysis → H_2
   Solar Energy → photovoltaic → water electrolysis → H_2
5. Hydrid → turbine generators → water electrolysis → H_2
6. Wind → turbine generators → water electrolysis → H_2
7. Coal → gasification → synthesis gas → H_2
8. Natural gas → reforming → synthesis gas → H_2

8. APU Concept

The way for rapid fuel cell commercialization is to overcome the lack of H_2 distribution networks.

The potential benefits are high efficiency generation of electricity,independence of engine condition (on, off, idle),zero or near zero emissions with on board generation (reduction of pollutants and green house gases emissions).

Reforming processes for on-board APU applications

8.1 POX Reaction

$$C_nH_m + n/2O_2 \rightarrow n\ CO + m/2\ H_2$$

It is exothermic,there is less hydrogen production with a lower concentration and dilution due to nitrogen present in the fed air .

8.2 SR Reaction

$$C_nH_m + nH_2O \rightarrow nCO + (n+m/2)H_2$$

There is higher hydrogen production with a higher concentration but external heat addition is necessary.

8.3 Autothermal Reforming

$$C_nH_mO_p + x(O_2+3.76N_2) + (2n-2x-p)H_2O \rightarrow nCO_2 + (2n-2x-p+m/2)H_2 + 3.76N_2$$

It combines in several ratios SR and POX reactions in the same unit, the exothermic POX drives the endothermic SR. The reaction products react with the remaining steam according to the exothermic WGS reaction equilibrium.

8.4 Catalytic Partial Oxidation of Natural Gas

$$CH4 + ½O_2 \rightarrow 2\ H_2 + CO \quad \Delta H = -35.6\ kJ\ mol^{-1}$$

The above reaction is slightly exothermic requiring lower energy consumption.

It requires more compact technology with lower investment cost.

It produces syngas with $H_2/CO = 2$ which is suitable for many important downstream processes such as Fischer-Tropsch synthesis.

8.5 Water Gas Shift Reaction (WGS)

$$CO + H_2O \rightarrow H_2 + CO_2 \quad \Delta H = -41.2\ kJ\ mol^{-1}$$

- High Temperature-WGS: 300-500°C
  Commercial catalyst: Fe/Cr oxides
- Low Temperature-WGS: 200-400°C
  Commercial catalyst: copper, zinc oxide on alumina

The parasite reactions are the Methanation reactions.

$$CO + 3\ H_2 \rightarrow CH_4 + H_2O$$
$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$$

Commercial catalysts disadvantages:

- Low activity and some thermodynamic limitations at high T for HT catalysis
- Pyrophoric characteristics for LT catalysis
- Time consuming pre-conditioning for start-up (reduction/ oxidation)

Hence, synthesis and characterization of new catalysts is required

9. Synthesis and characterization of CATs for CO clean-up

Catalyst preparation methods:
1. IWI (Incipient Wetness Impregnation)
2. SCS (Solution Combustion Synthesis)
3. DP (Deposition-Precipitation)

Catalyst analysis methods:
1. XRD
2. HRTEM
3. SEM-EDS
4. BET area

9.1 Reformate clean-up second step: CO Preferential Oxidation reaction

$CO + ½ O_2 \rightarrow CO_2$
Conversion reaction
Exothermic reaction: - 283 kJ/mol
1st generation catalysts required for reaction:
Active elements: Pt, Rh, Ru, Pd
Supports: Al2O3 and 3A, 4A, 5A zeolites

9.1.1 CO-PROX Advantages

It is reliable to remove CO down to 10 ppmv and Working temperatures similar to those of PEMs: heat exchanger is not necessary in upstream stack inlet.

9.1.2 CO-PROX Disadvantages

It requires high H_2 consumption: 3-4 mol H_2 / mol CO to produce water. There is appreciable heat loss at low temperature from the reactor, then thermo-dynamically of low usefulness for FPU, careful O_2 dosage, therefore unsuitable for low power FPU (expensive MFM are needed), careful temperature control.

9.2 Reformate clean-up alternative 2nd step: CO Selective METhanation reaction

$CO + 3 H_2 \rightarrow CH_4 + H_2O$

Conversion reaction
Exothermic reaction: - 206.2 kJ/mol

Parallel reactions
$CO_2 + 4H_2 \rightarrow CH_4 + 2 H_2O$
Parallel reaction: CO_2 methanation
Exothermic reaction: - 164.9 kJ/mol

9.2.1 CO-SMET Advantages

Reliable to remove CO down to 10 ppm, no co-reactant addition, no dosing system. For integrated FPU-PEM stack, the produced CH_4 burnt with anode exhaust generates about 50% more heat compared to CO-PROX at high temperature, thermodynamically usefulness for FPU reformer FPU efficiency increase. Heat loss at low temperature (thermo-dynamically less interesting for FPU) about 25% that of CO-PROX. Easier temperature controllability: lower heat generated in the reactor (about 75% less than that in CO-PROX)

9.2.2 CO-SMET Disadvantages

The Working temperatures higher than those of PEMs: heat exchanger necessary upstream stack inlet ,higher than CO-PROX H_2 consumption: 4-6 mol H_2 / mol CO (1-3 mol H_2 / mol CO to produce water). For the same power stack, about 3% more H_2 produced toward FPU efficiency decrease.

10. H_2 crossover studies

When O_2 and H_2 permeate through the membrane and react directly with each other, the energy is lost as heat due to inefficiency of the fuel cell. Moreover, O_2 and H_2 crossover leads to the formation of peroxide and hydroperoxide radicals leading to further deterioration of the membrane. Increasing of H_2 crossover is a sign of MEAs deterioration. H_2 crossover current densities rise by decreasing the thickness of the membranes and increasing the operative cell temperatures.

Thus though still riddled with problems, the concept of hydrogen economy and research towards the same is indeed a continuous process.