**Molten Carbonate Fuel Cells (MCFC)**

Operating temp = 500 - 700 deg C

MCFC is approaching the stages of commercialization 250kW-2 MW power generation. For large scale power plants.

Fuels: hydrogen, reformed natural gas of gasified cola

Electrolyte: molten carbonate

**Advt of high temperature**:

1. internal reforming of the fuel is possible – simplifies the design of MCFC
2. favourable for fuel oxidation and oxidant reduction allowing the selection of electrode materials like Co or Ni instead of Pt.
3. permit the co-generation of heat and electricity
4. polarization losses are minimum , leads to higher efficiency

 Cell reaction : lecture notes and text

Functions of carbon dioxide:

Carbon dioxide is produced by the anodic reaction and is used up in the cathodic reaction.

Alternatives

fuels: methanol, syngas(carbon monoxide + hydrogen)

oxidants: carbon dioxide + air (30-70 mixture)

melt has an invariable composition, carbonate and carbon dioxide participates in the reaction

Cell emf: lecture notes and text

Use of methane and methane reforming: lecture notes and taxt

Principles of MCFC operation

1. electrons are transferred from anode to cathode via the external circuit where they participate in reduction reaction.
2. The charges are conducted by the carbonate anions from the cathode through the molten electrolyte to the anode
3. Carbon dioxide the recycled from the anode to the cathode using “carbon dioxide transfer device” or more conveniently by withdrawing the anode ext gas formed by complete combustion and mixing it with cathode gas stream.

MCFC-PAFC comparison: lecture notes and text

Cell components: lecture notes and text

**Electrolyte and matrix**

Electrolyte: a mixture of alkali molten carbonates

Lithium carbonate + sodium carbonate is more advantageous than lithium carbonate + potassium carbonates as it has

1. higher ionic conductivity
2. higher cell performance
3. lower volatility

Addition of alkaline earth metal carbonates (Ca, Sr, Ba)

1. disadvt: decreases the ionic conductivity of the melt
2. advt: increases the basicity, loweruing the NiO solubility

**Electrolyte support**

1. mixture of ceramic particles that form the capillary network which contains the electrolyte
2. does not participate in the electrochemical process
3. the support materials control the physical properties (thermal strength and differential pressure capabilities) of the matrix
4. governs the electrolyte retention volume and ohmic resistance of the matrix
5. sub-microsized gamma lithium aluminate is used as the support in coarse, fibrous and fine forms.
6. Composition:

fine particle: gamma lithium aluminate 0.1micrometer 55%

course particle: alpha alumina 100 micrometer 30%

fiber: alpha alumina 5 micrometer 15%

**Cathode material**

NiO

Essential conditions for cathode materials:

1. high electrical conductivity
2. high mechanical resistance
3. low solubility in molten carbonate

Ni gets oxidized to NiO and gets lithiated insitu during the first hours of cell operation. This increases the porosity

Mechanism of NiO formation: lecture notes and text

Lithium incorporation is an oxidation reaction. For every lithium on nickel 3+ ion is formed. Micropores of 1 micrometer diameter are formed near to the original pores of 6-10 micormeter diameter in the initial structure

**Dissolution of NiO (Main concern in MCFC)**

1. the ions gets transported to the anode and is reduced to metallic nickel and deposits on the matrix
2. this causes electronic short circuit and loss of power output
3. leads to syructiral deterioration of the cathode
4. NiO solubility decreases when basicity of the electrolyte due to oxide ions increases due to common ion effect
5. Basicity of lithium carbonate >sodium carbonate > potassium carbonate. So solubility of NiO is least in lithium carbonate – sodium carbonate mixture
6. Addition od alkaline earth metal carbonates increases the basicity of the electrolyte, decreasing NiO solubility
7. In basic conditions, different dissolution products can be generated

**Anode materials**

porous Ni + 10% Cr

The pores are smaller than that of cathode

Role: electrocatalytically oxidize the fuel

Parameter: pore diameter 3-5 micrometer; porosity: 55-70%; surface area: 0.1-1 m2/g and thickness: 0.5-0.8 mm

Challenge: instability leading to pore growth and loss of surface area

Solution: addition of 2-10% Cr

Action: formation of chromium trioxide followed by surface formation of lithium chromate: prevents surface area loss. Disadvt: modification of surface characteristics

A thin layer of Ni-LiAlO2 on the surface of the anode prevents gas leakage

**Interconnection plates**

Bipolar plates separate the cathode from the adjacent anode in a fuel cell stack containing several individual cells

Material: Cr-Ni-ferrite stainless steel

Function: all the bipolar plates constitute the gas distribution network

Aluminization prevents the corrosion of the bipolatr plates

**Lifetime limiting issues of MCFC**

1. dissolution of NiO cathode: mechanism: lecture notes and text
2. corrosion of bipolar plates
3. electrolyte retention capacity
4. catalyst deactivation
5. matrix cracking
6. electrolyte losses due to wetting of cell components, lithiation of electrodes, vapourization of potassium carbonate. Chief loss of electrolyte is during the first 1000 h of cell operation
7. contamination by sulphur or chlorine compounds

**Direct methanol fuel cell (DMFC)**

**Promising candidate for**

1. portable power sources
2. electric vehicles
3. transportation applications

**Fuel**: methanol

**Advt**: low cost, easily stored and handled, readily available and soluble in aqueous electrolytes, high calorific value

**Availability**: from oil, natural gas, coal or biomass

**Indirect vs direct**:

In indirect MFC methanol is foirst reformed to hydrogen at ahigh temperature while in DMFC, methanol is oxidized directly at the anodic compartment

In vehicles: if used in vehicles (operating temp 60-80 deg C) emissions will e considerably lower than IC engines. Only carbon dioxide and water are emitted.

Cell reactions and figure: lecture notes + text

**DMFC vs gas-feed fuel cells**

1. elimination of fuel vapourizer and its associated gas controls
2. elimination of complex thermal management systems
3. dual purpose use of methanol/water as fuel + coolant
4. lower size, weight and temperature of the system

**Catalyst**: platinum

This is the major constraint in DMFC in promoting DMFC to power vehicles. Although Pt can be recovered after the vehicle’s lifetime, still large amounts of Pt will be needed for the large scale production of vehicles. This is not available at present. Solving this problem is important for DMFC to ssisst in a progress towards sustainable transportation sector.

**Major drawbacks of DMFC**

1. very high cost
2. acid electrolytes needed due to carbonate formation at the desirable current densities – acid electrolyte cause corrosion
3. anode reaction is slow, so a large overpotential is encountered
4. platinum catalyst is easily attacked by impurities and by the products of anodic reactions

**Milestones in DMFC Technology**

First demonstration of hydrogen-air fuel cell was by William Grove in 1839, In modern times it was Francis Bacon (1992) who’s work culminated in the use of hydrogen-air fuel cell in Apollo space programme and resulted in diversification into AFC, MCFC, SOFC and solid polymer electrolyte technologies

DMFC was pioneered by Shell company along with Exxon, France during 1960’s and 1970’s. Shell used sulphueic acid as the electrolyte.

MCFC electrode prep by Shell group

1. A thin electrode with finely spaced pores were formed by evaporation of silver or gold onto a substrate PVC.
2. A layer of catalyst is then attached to this metallic layer

Later developments

1. Catalyst: Pt-Ru alloy
2. Alkaline and buffer electrolyte

The drop in oil prices during 1980’s pushed the cost of methanol-air fuel cell further. 1981 Shell ceased all research on DMFC

DMFC again became important when the global environmental issues sprang up

The car manufacturers Benz Ford, General Motors and Toyota are actively involved in development of vehicles powered by fuel cells

Chief problem is still catalysis

Requirement of Pt is still 10 times the total amount of Pt being mined. Catalytic coverters (which has Pt but very less amount) are not required in fuel cells is n advantage of fuel cells

**Advantages associated with DMFC technology**

1. Pt is more than 95% recoverable at low cost. So the actual cost of DMFC = money required to purchase the catalyst during its life-time + money required for recovering the catalyst
2. There is a substantial scope for improving the electrocatalyst in DMFC

It can be concluded that neither the limited supply of Pt nor the cost problem is serious so as to hamper the growth of R & D in MCFC

**Electrooxidation of methanol**

Methanol is adsorbed onto the Pt catalyst dissociatively with release of hydrogen. This reaction does not happen completely. Side products formed can be completely oxidized only at higher potentials. In acid medium only Pt and Pt vased catalyst can adsorb methanol.

**Steps in adsorption (details refer text and lecture notes)**

1. electrosorption of methanol onto Pt
2. oxidation of surface bound intermediates