UNIVERSITÀ DEGLI STUDI DI TRIESTE

Dipartimento di Ingegneria e Architettura

FUEL CELL TECHNOLOGIES

– PART 3 –

Prof. Marco Bogar

A.A. 2023-2024

OUTLINE

1. Solid Oxide Fuel Cells
2. Direct Methanol Fuel Cells*
3. Unitised Regenerative Systems

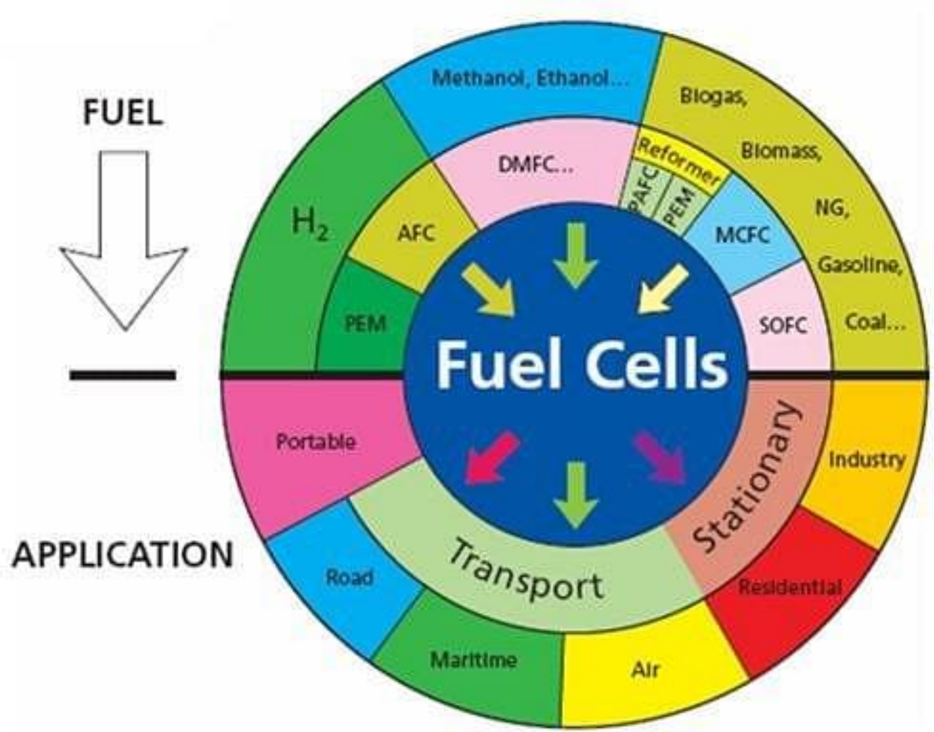
* Topic not asked at the exam

BIBLIOGRAPHY

Reference	Paragraph/Pages
Fuel Cell Systems Explained, Andrew L. Dicks, David A. J. Rand, (2018), Wiley	Ch. 9 (up to 9.5)~~, and 6.1~~
Fuel Cell Engines, Mench M. M., (2008), Wiley	Ch. 7.1~~, and 6.4~~
Hydrogen production by electrolysis, Agata Godula-Jopek, 2015 Wiley	Ch. 5

Insights	
R4	Sing M. et al., Solid oxide fuel cell: Decade of progress, future perspectives and challenges, International Journal of Hydrogen Energy, 46, (2021), 27643-27674; DOI: https://doi.org/10.1016/j.ijhydene.2021.06.020
R5	Berretti E. et al., Direct Alcohol Fuel Cells: A Comparative Review of Acidic and Alkaline Systems, Electrochemical Energy Reviews (2023) 6:30; DOI: https://doi.org/10.1007/s41918-023-00189-3
R6	Weber A. Z. et al., Redox flow batteries: a review, Journal of Applied Electrochemistry, 41, (2011), 1137-1164; DOI: 10.1007/s10800-011-0348-2

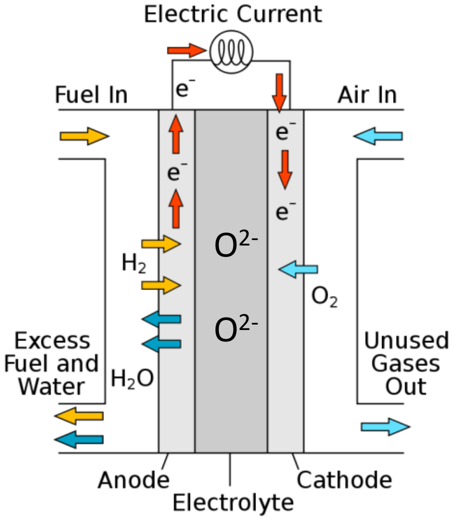
INTRODUCTION



https://collegedunia.com/exams/fuel-cells-chemistry-articleid-152

1. SOLID OXIDE FUEL CELLS

SOLID OXIDE FUEL CELLS



https://en.wikipedia.org/wiki/Solid_oxide_fuel_cell

Anode	$2H_2 + 2O^{2-} \rightarrow 2H_2O + 4e^-$
Cathode	$O_2 + 4e^- \rightarrow 2O^{2-}$
Overall	$2H_2 + O_2 \rightarrow 2H_2O$

- SOFC are a completely solid-state device operating thanks to an oxide ion-conducting ceramic material as the electrolyte.
- The ionic conduction is carried out via the O^{2-} anion
- The can be fed with different fuels such as H_2 or CH_4, in example.
- By operating at high temperatures (between 700 and 1000 °C, even if novel technologies allow to reduce operating temperature to about 600 °C)
- Precious metal catalysts are not needed, but materials with similar thermal expansion coefficients need to be used.

SOLID OXIDE FUEL CELLS – THE ELECTRODES

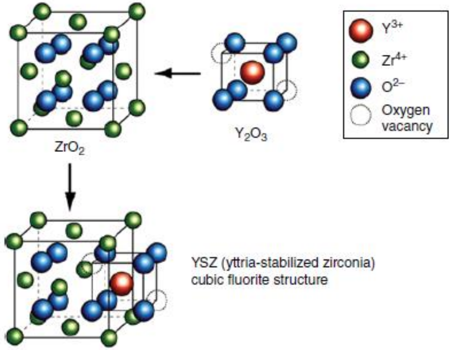
Electrode	Materials	Properties
Anode	• Standard: cermet composed by yttria-stabilized zirconia and nickel (Ni-YSZ) • Possible improvements: nickel-gadolinium doped ceria (NGC), offering the possibility to operate at lower temperatures.	• Good electronic conductivity and resistant under chemically reducing condition • Ni is further resistant to S poisoning • Requires 20 – 40 % porosity to facilitate the gas flow
Cathode	• Standard: ceramic compounds are used (such as strontium-doped lanthanum manganite (LSM), $La_{1-x}Sr_xMnO_3$ in example). Material research is still ongoing (i.e. perovskites)	• It must possess sufficient porosity to facilitate the oxygen gas flow

SOLID OXIDE FUEL CELLS – THE ELECTROLYTE

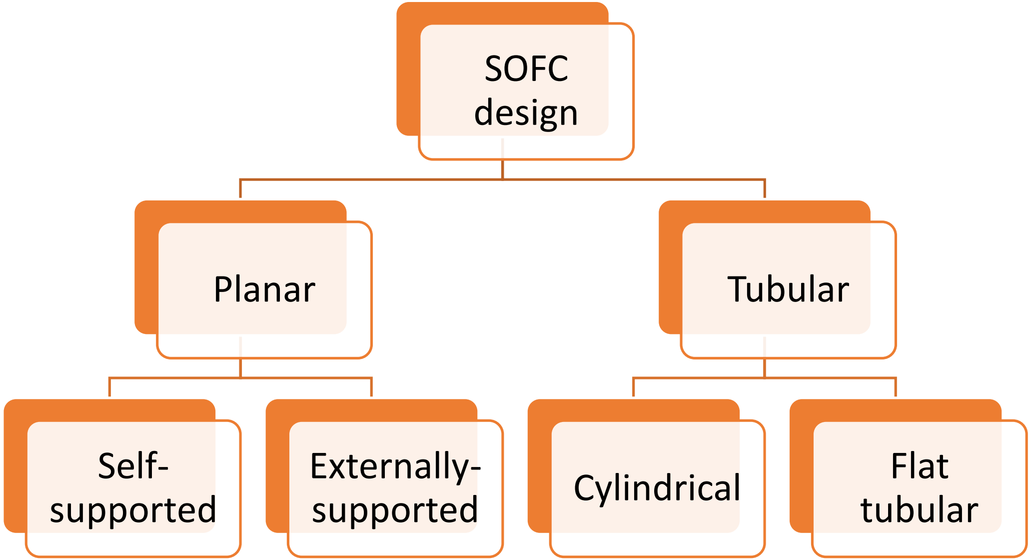
Being exposed to both oxidizing (air side) and reducing (fuel side) species at high temperatures, to ensure long-term operation the electrolyte needs to satisfy the following properties:

- Sufficient ionic conductivity to minimize ohmic loss and with little electronic conductivity.
- Mechanical compatibility with both electrodes (thermal expansion coefficients, must match at the interfaces).
- Chemical stability to both oxidation and reduction processes.
- A dense structure, i.e., impermeable to gas.

To date, YSZ constitutes the standard material to be used.



SOLID OXIDE FUEL CELLS – DESIGN



SOFC design

Planar

Tubular

Self-supported

Externally-supported

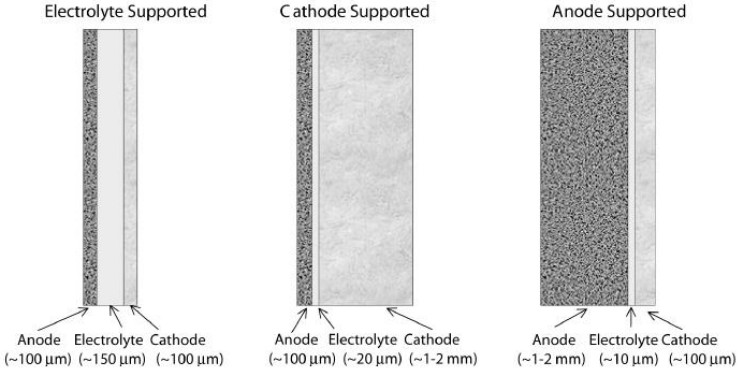
Cylindrical

Flat tubular

SOLID OXIDE FUEL CELLS – DESIGN

Planar design / Self-supported SOFC

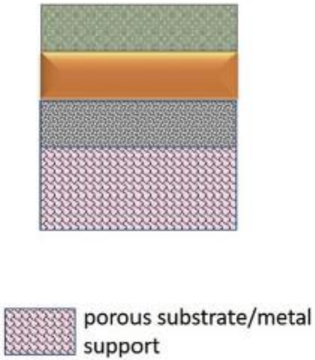
One of the three main layers of the SOFC is mechanically supporting the entire electrochemical cell. The main issue concerns the fact that each electrode has its own optimal thickness. In example electrolyte thickness have to balance mechanical resistance, avoidance of crossover phenomena and maximise ionic conduction.



SOLID OXIDE FUEL CELLS – DESIGN

Planar design / Externally-supported SOFC

A porous (metal) substrate is used to provide mechanical support for the electrochemical cell. Such configuration allows to optimize the geometrical design of the supported layers, but has to satisfy the constraints of high mechanical strength, excellent electrical conduction, high thermal conduction distribution, and possess thermal expansion coefficient well matching with other fuel cell materials.



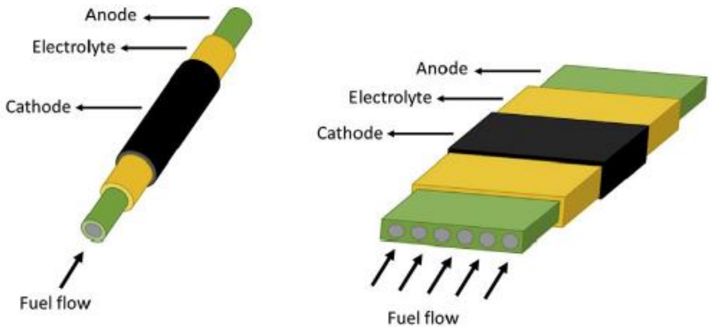
SOLID OXIDE FUEL CELLS – DESIGN

Tubular and flat tubular geometries

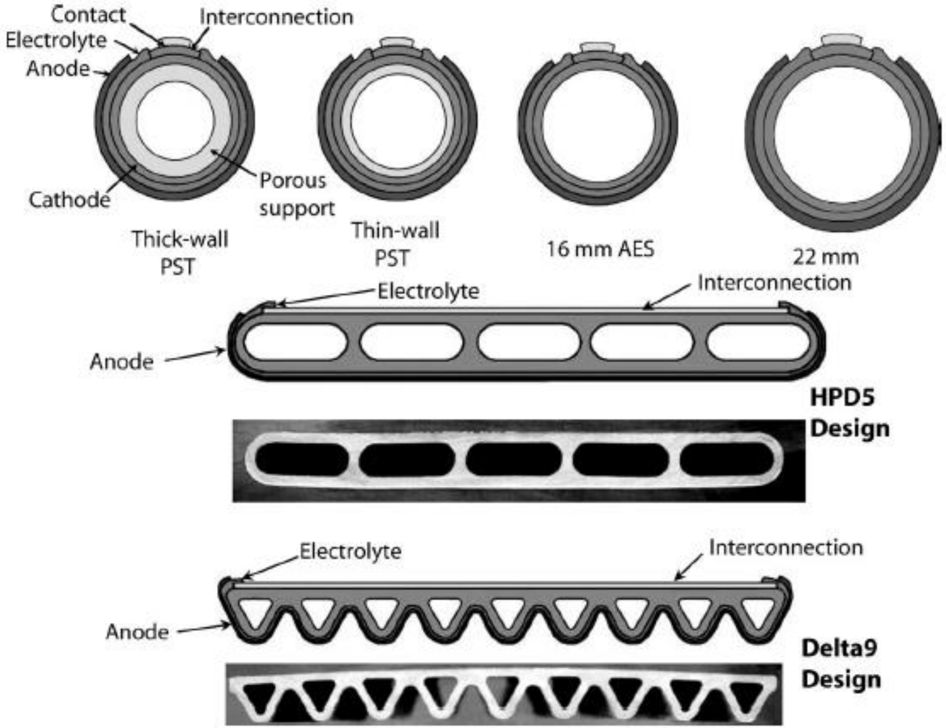
They are considered one of the most effective approaches to enhance the volumetric power densities, which can be improved by reducing the cylinder section area. Moreover, they allow to avoid using high-temperature interconnecting and sealing as planar architecture needs, and to finely tune the oxidizing supply.

To date, the optimal tube diameter is set below 10 mm on anode supported SOFC, as this architecture allows to achieve good mechanical strength and electrical conductivity.

There is still lot of research carried out for improving fabrication methods and the overall design at the microscale.



SOLID OXIDE FUEL CELLS – DESIGN



SOLID OXIDE FUEL CELLS – DESIGN

Configuration	Advantages	Disadvantages
Planar	High power density Low manufacturing costs	Limited mechanical strength High temperature sealing is required
Tubular	High mechanical strength High temperature sealing is not required	Lower power density (due to higher internal ohmic losses) High manufacturing cost

SOLID OXIDE FUEL CELLS – SUMMARY

Advantages:

- Efficient, as the advantages of catalysing the reaction with temperature are exploited, overall reflecting in a reduction of activation losses. This allows to operate without precious metal catalysts
- Tolerant to CO and CO_2
- Suitable to be used in complex systems where heat recovery can be exploited, as the overall system efficiency can be set about 80%.
- Suitable to be used with several fuels

SOLID OXIDE FUEL CELLS – SUMMARY

Disadvantages:

- Production costs are still high, due to the lack of a standard production method (and for some parts also for a standard material)
- Not suitable for operating with transient loads
- Thermal stability is as important as chemical one, as thermal stresses have a remarkable impact on cell and stack lifetime, which is still one of the major limits for this technology
- Strict requirements for interconnects and sealants in planar design can be problematic
- Start-up times are long

2. DIRECT METHANOL FUEL CELLS

DMFC - INTRODUCTION

Direct Methanol Fuel Cells (DMFC) are a class of fuel cells which can be described as direct liquid fuel cells, generating electricity by oxidizing a liquid fuel. Most of these fuel cell devices use elements from PEM technology. Direct Methanol Fuel Cells represent the most mature component of this class of devices.

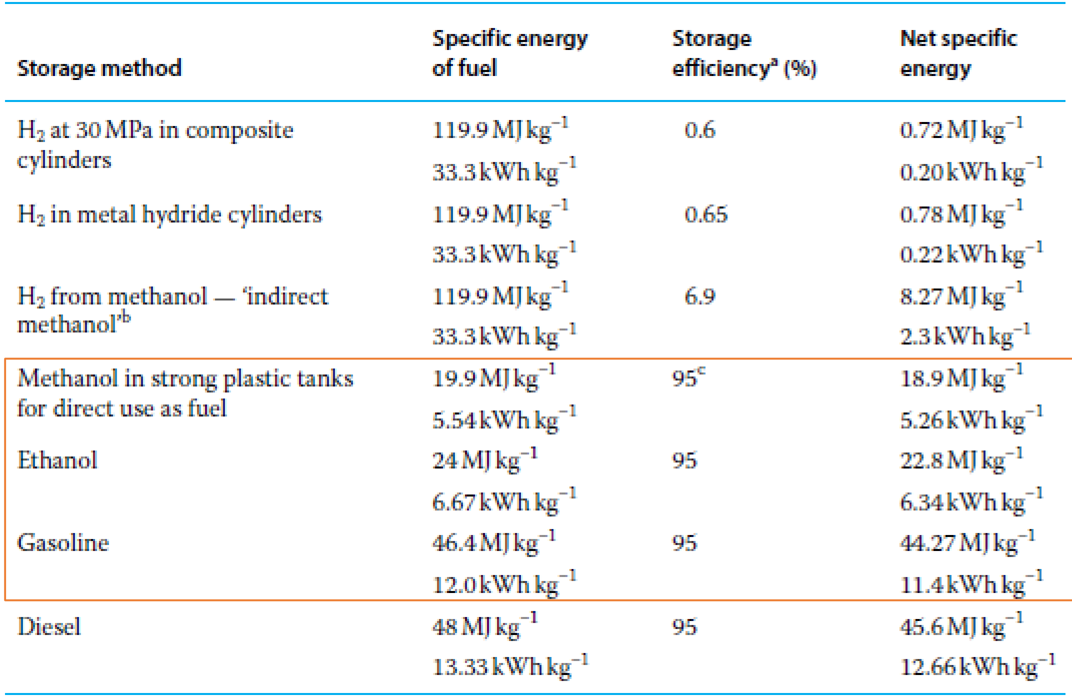
DMFC were considered a viable option for commercial devices in between the 1960s and 1970s, before the establishment of the PEMFC technology.

Moreover, this device is presented to remind as hydrogen is not the only fuel which can be used for feeding fuel cell systems and many alcohols (such as ethanol or propanol), or organic liquids (as formic acid or ethylene glycol in example) would be suitable for being processed in fuel cell systems. In particular, ethanol (CH_3CH_2OH) was found interesting because less toxic than methanol.

DMFC - INTRODUCTION

DMFC process methanol (CH_3OH), an alcohol miscible with water, characterized by a boiling point of 64.7 °C, with half of the gravimetric specific energy of gasoline and easy to be reformed into hydrogen. Its high specific energy is related to its physical state, which makes methanol more convenient than hydrogen in terms of storage.

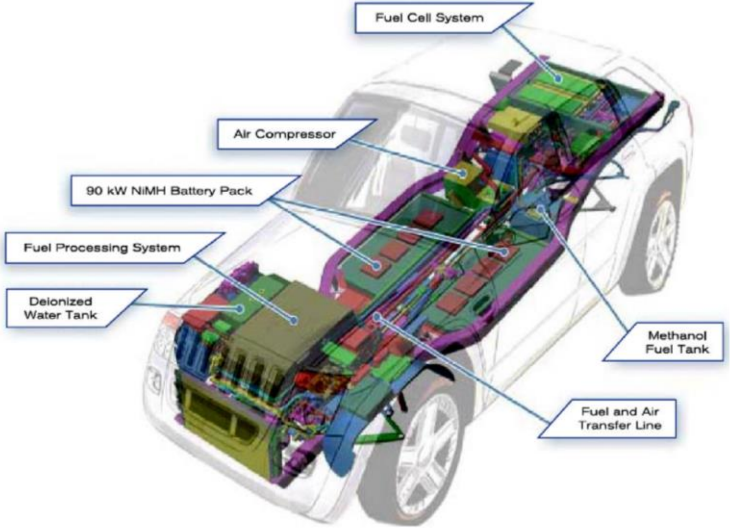
Moreover, by directly oxidising methanol the reformation step could be skipped.



Storage method	Specific energy of fuel	Storage efficiency[a] (%)	Net specific energy
H_2 at 30 MPa in composite cylinders	119.9 MJ kg^{-1} 33.3 kWh kg^{-1}	0.6	0.72 MJ kg^{-1} 0.20 kWh kg^{-1}
H_2 in metal hydride cylinders	119.9 MJ kg^{-1} 33.3 kWh kg^{-1}	0.65	0.78 MJ kg^{-1} 0.22 kWh kg^{-1}
H_2 from methanol — 'indirect methanol'[b]	119.9 MJ kg^{-1} 33.3 kWh kg^{-1}	6.9	8.27 MJ kg^{-1} 2.3 kWh kg^{-1}
Methanol in strong plastic tanks for direct use as fuel	19.9 MJ kg^{-1} 5.54 kWh kg^{-1}	95[c]	18.9 MJ kg^{-1} 5.26 kWh kg^{-1}
Ethanol	24 MJ kg^{-1} 6.67 kWh kg^{-1}	95	22.8 MJ kg^{-1} 6.34 kWh kg^{-1}
Gasoline	46.4 MJ kg^{-1} 12.0 kWh kg^{-1}	95	44.27 MJ kg^{-1} 11.4 kWh kg^{-1}
Diesel	48 MJ kg^{-1} 13.33 kWh kg^{-1}	95	45.6 MJ kg^{-1} 12.66 kWh kg^{-1}

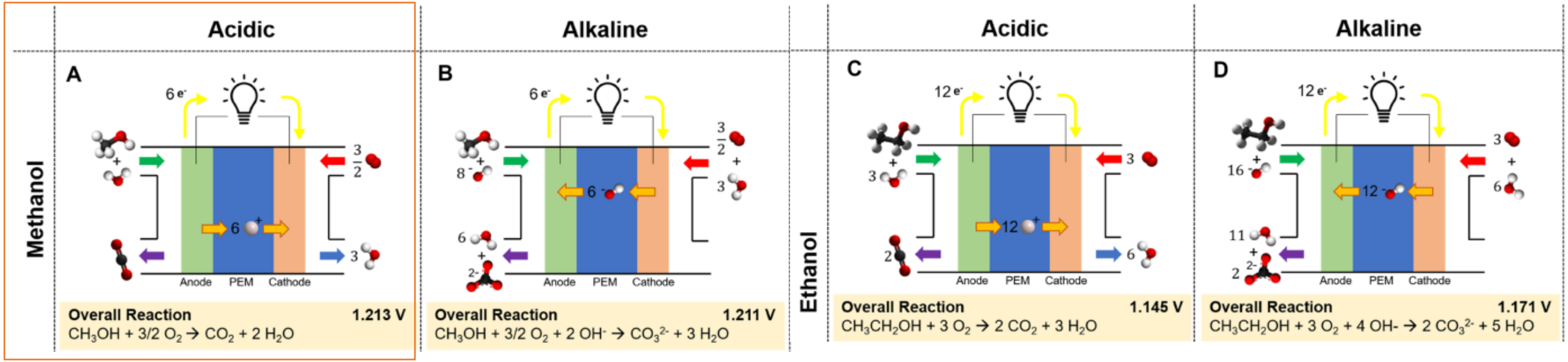
DMFC - INTRODUCTION

In DMFC (as for DAFC) fuel is fed within the fuel cell in liquid form, while air is supplied as an oxidiser. Moreover, by directly oxidising methanol, these technology allows to skip the reformation step. To exploit this property, some demonstration car types were realised in the first years of the new millennium.



Tran D. , SERIES 2001-01-2508 Development of the Jeep Commander 2 Fuel Cell Hybrid Electric Vehicle, (2001)

DMFC - INTRODUCTION



Berretti E. et al., Electrochemical Energy Reviews (2023) 6:30

DMFC – COMPOSITION

Electrolyte

Polymeric membranes are used as an electrolyte. In addition to the features already seen for such a component, chemical stability has to be guaranteed at operating temperatures bigger than 80°C.

As well as, Nafion, Nafion-like (different side chains), sulfonated polyether ether ketone (sPEEK), polybenzimidazole (PBI), or composite membranes can be used.

DMFC – COMPOSITION

Anode

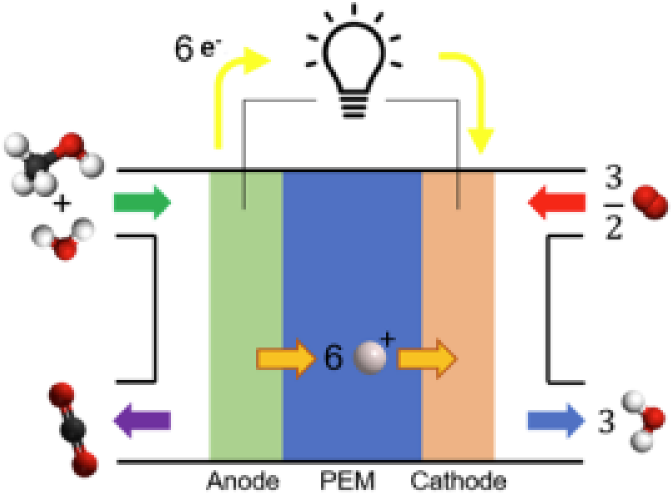
Catalyst materials entitled to deal with the MOR are based on noble metals, such as Pt and its alloys: to date PtRu alloy represent the state of the art for this technology, because Ru catalyses the formation of CO_2 from C-based precursors. Nonetheless, the presence of Pt makes the electrode still suitable to be poisoned by the CO.

In the last years research is experimenting the synthesis of multiple-component electrocatalysts, such as PtRuM and $PtMO_2$, with M a transition metal as in example Ti, V, Mn, W, Ni, Mo, to increase reaction efficiency.

Cathode

For the ORR standard Pt/Carbon catalyst is used.

DMFC – PRINCIPLES OF OPERATION

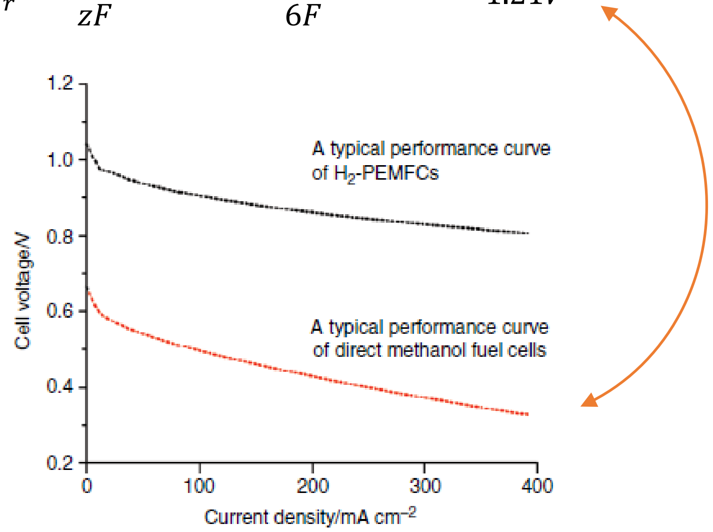


Anode (MOR)	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$	$E^0 = 0.016\ V$
Cathode (ORR)	$3/2\ O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$	$E^0 = 1.229\ V$
Overall	$CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 3H_2O$	$E^0 = 1.213\ V$

Berretti E. et al., Electrochemical Energy Reviews (2023) 6:30

The overall reaction in DMFC is a six-electron-transfer reaction, consequently:

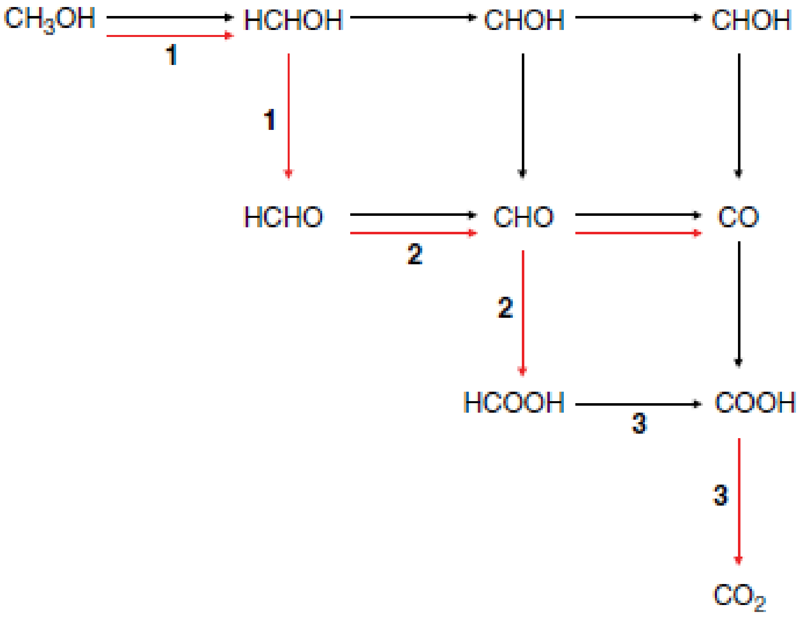
$$V_r^0 = \frac{\Delta \bar{g}_f^0}{zF} = \frac{698.2\ * 10^3\ J\ mol^{-1}}{6F} = 1.21V$$



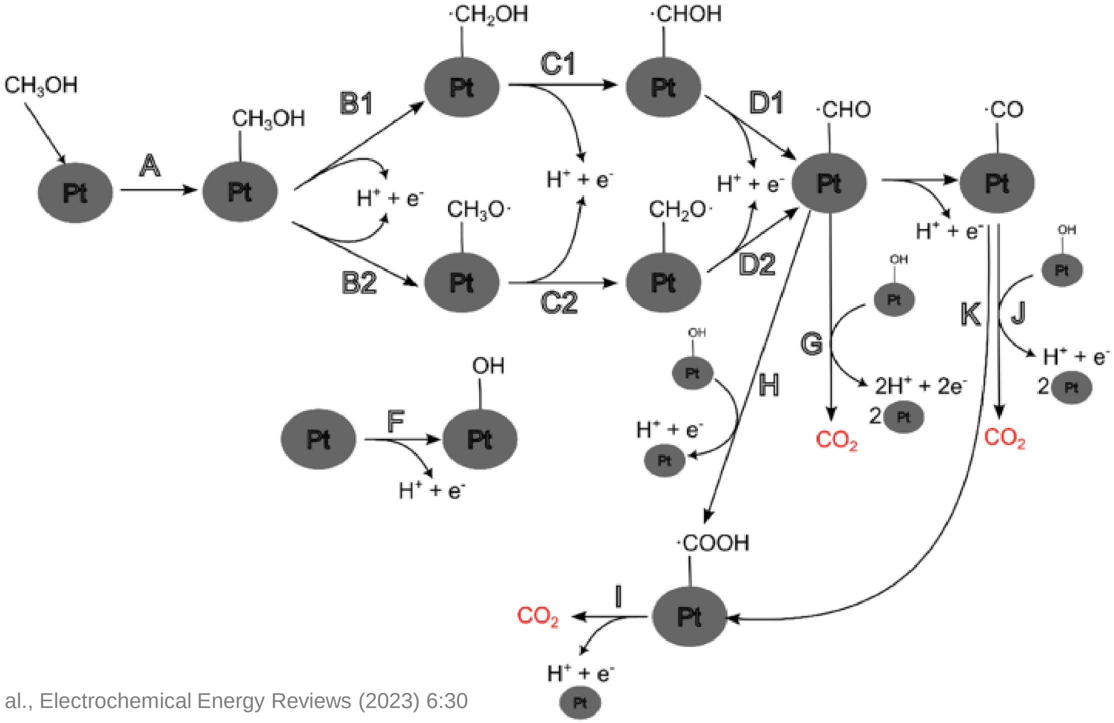
DMFC – PRINCIPLES OF OPERATION – LIMITATIONS

Reaction kinetics of MOR at the anode constitute one of the main limitations reducing DMFC performances. In fact, reaction kinetics are much slower than for HOR in PEMFC (using the same MEA), due to the higher number of steps in which the reaction evolves, reducing the overall reaction rate. This leads to the production of about 0.25 A cm^{-2}, operating at 0.4 V.

Furthermore, along the reaction paths, carbon monoxide formation is possible, leading to CO poisoning of the catalyst, thus influencing the catalyst choice.

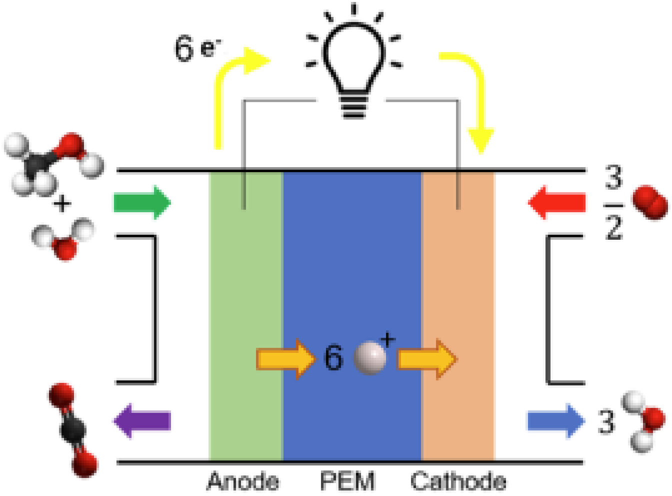


DIRECT METHANOL FUEL CELLS



Berretti E. et al., Electrochemical Energy Reviews (2023) 6:30

DMFC – PRINCIPLES OF OPERATION – LIMITATIONS



Anode (MOR)	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$
Cathode (ORR)	$3/2\ O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$
Overall	$CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 3H_2O$

Berretti E. et al., Electrochemical Energy Reviews (2023) 6:30

Another issue is related to **fuel crossover**, crucial when PFSA membranes are used as electrolytes: in fact the water paths forming into PFSA membranes constitute routes promoting methanol diffusion and consequent absorption in the electrolyte. Consequent migration to the cathode leads to reduction of open circuit voltage.

Apart from lowering the operating potential, methanol crossover at the cathode makes occur MOR also at the cathode, catalysed by the presence of Pt (even if with low reaction rates), further deteriorating fuel cell performances.

To date, no suitable solutions were found to replace Pt cathodic catalyst.

DMFC – SUMMARY

Advantages

- Liquid fuels do not require separate cooling or humidification subsystems.
- Methanol is highly dense liquid at ambient pressure, eliminating problems with fuel storage volume.
- No reformation / hydrogen production systems would be needed.
- Methanol is ubiquitous and transportable exploiting an already existing infrastructure.

DMFC – SUMMARY

Drawbacks:

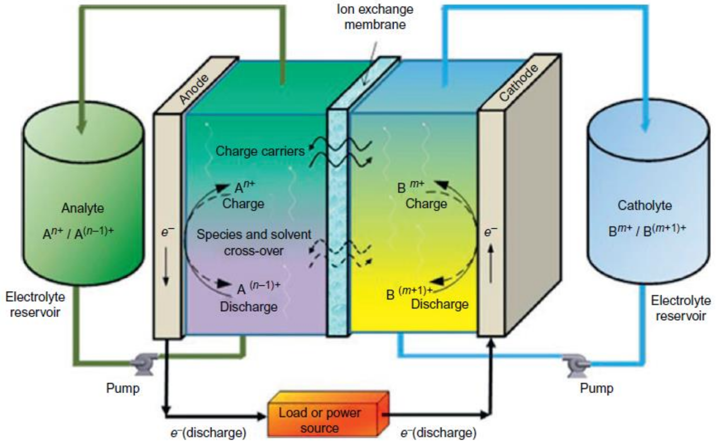
- Water Management is critical and adequate performances can be hardly ensured, as methanol is supplied in water solution at the anode side and cathode flooding is more likely to occur.
- Methanol crossover is still critical to be limited, greatly reducing the open-circuit voltage of the DMFC from the theoretical value of ~ 1.2 V to around 0.7 – 0.8 V.
- Poor anode kinetics are intrinsically characterising the MOR
- Counterflow and removal of carbon dioxide needs to be accounted as it also forms a counterflow in overall anode mass transport
- Methanol is slightly toxic, spreads more easily into the ground than gasoline, and is highly flammable and miscible in water so that contamination with reservoirs is very simple.

UNITISED REGENERATIVE SYSTEMS

REDOX FLOW BATTERIES

Redox Flow Batteries are large-scale energy storage devices, consisting of two compartments separated by an ion exchange membrane. Each compartment is connected with a reservoir tank and a pump, forming an electrolytic circuit.

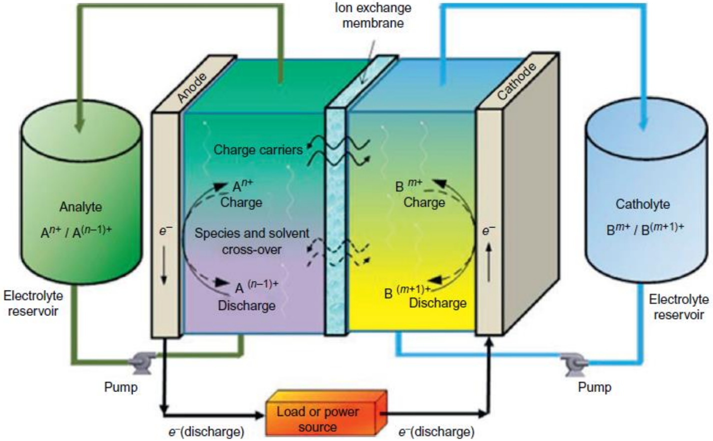
Anode and cathode electrons are thus flown by these two electrolytes (respectively called analyte and catholyte) and, by exploiting the occurrence of two couples of different redox reactions, evolving at the electrodes surface.



Weber A. Z. et al., J. Appl Electrochem (2011) 41:1137–1164

REDOX FLOW BATTERIES

The active species are oxidized or reduced and the generated electrons flow through an external circuit. To maintain the neutrality of all electrolytes, ions from the supporting electrolyte cross a membrane to the other side of the device. During a charge or a discharge process, two main reactions are involved.

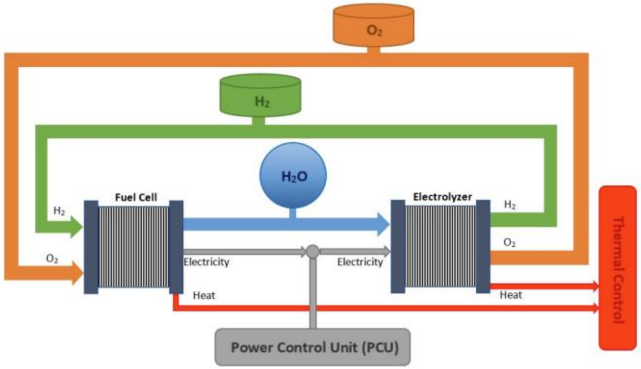


Weber A. Z. et al., J. Appl Electrochem (2011) 41:1137–1164

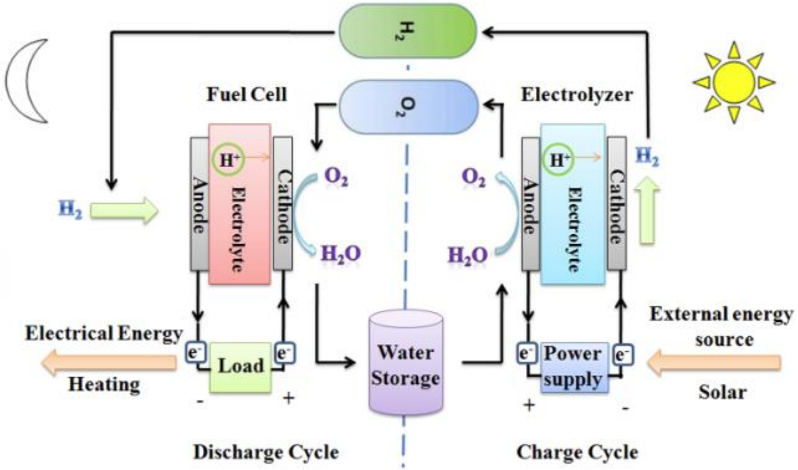
	Charge	Discharge
Negative electrode	$A^{n+} + xe^- \to A^{(n-x)+}$	$A^{(n-x)+} - xe^- \to A^{n+}$
Positive electrode	$B^{m+} - ye^- \to B^{(m+y)+}$	$B^{(m+y)+} + ye^- \to A^{m+}$

UNITISED REGENERATIVE FUEL CELL SYSTEMS

Unitized regenerative systems have been are thought to adapt the redox flow batteries architecture to water-hydrogen-oxygen systems. In principle, such a purpose could be achieved by building up a system combining an electrolyzer and fuel cell, within URFC systems water electrolysis and the fuel cell stacks are wanted to be integrated into a single unit able to operate reversibly.



Brey J. et al., E3S Web of Conferences 16, 17004 (2017)

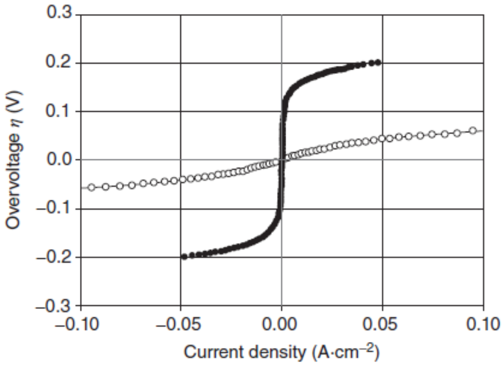


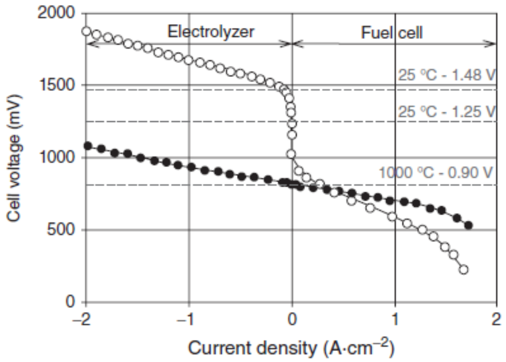
Pu Z. et al., Applied Energy 283 (2021) 116376

UNITISED REGENERATIVE FUEL CELL SYSTEMS – PROCESS REVERSIBILITY

In order to guarantee the operation of the device, it is mandatory to develop a MEA able to sustain both HER and HOR from one side and OER and ORR from the other.

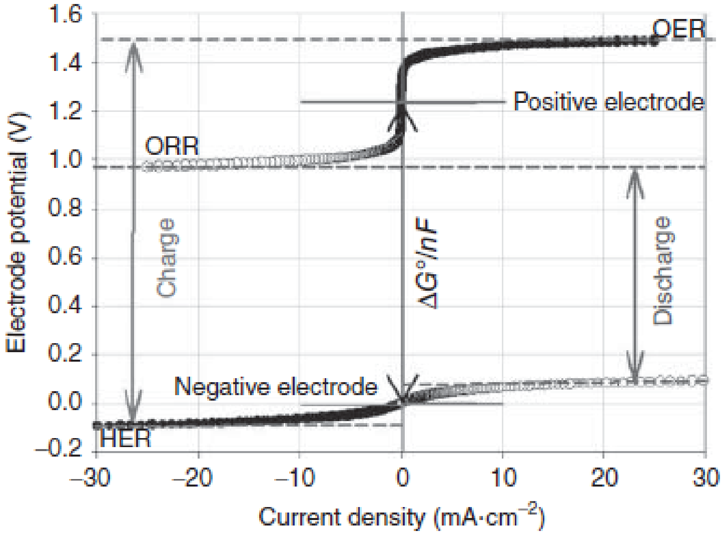
Catalyst selection is here crucial to develop flexible and efficient devices for sustaining the reversibility of the process, as the capability to reverse the process is related to the amount of current flowing through the circuit, together with the operating temperature.





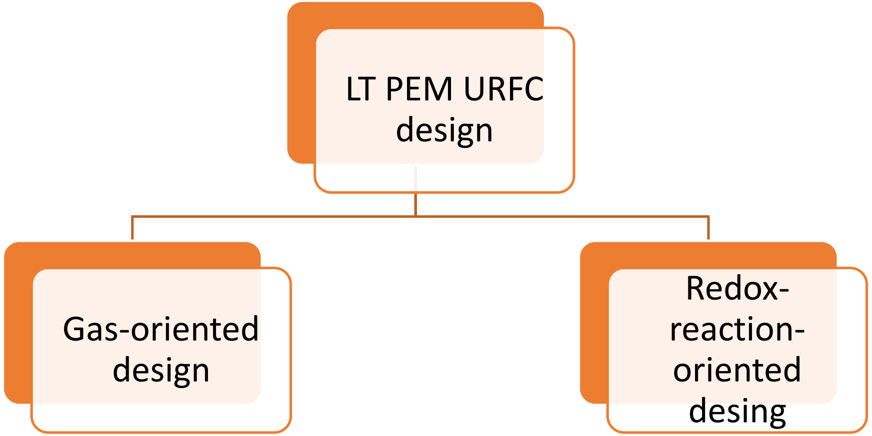
UNITISED REGENERATIVE FUEL CELL SYSTEMS – PROCESS REVERSIBILITY

The main limitation is due to shift in between OER and ORR, which is more irreversible as the hydrogen redox reactions.



LOW TEMPERATURE PEM URFC – DESIGN

Two approaches can be used to realize LT PEM URFCs: anode and cathode compartments can be designed to operate specifically with one gas or to operate with a specific redox process.



LT PEM URFC design

Gas-oriented design

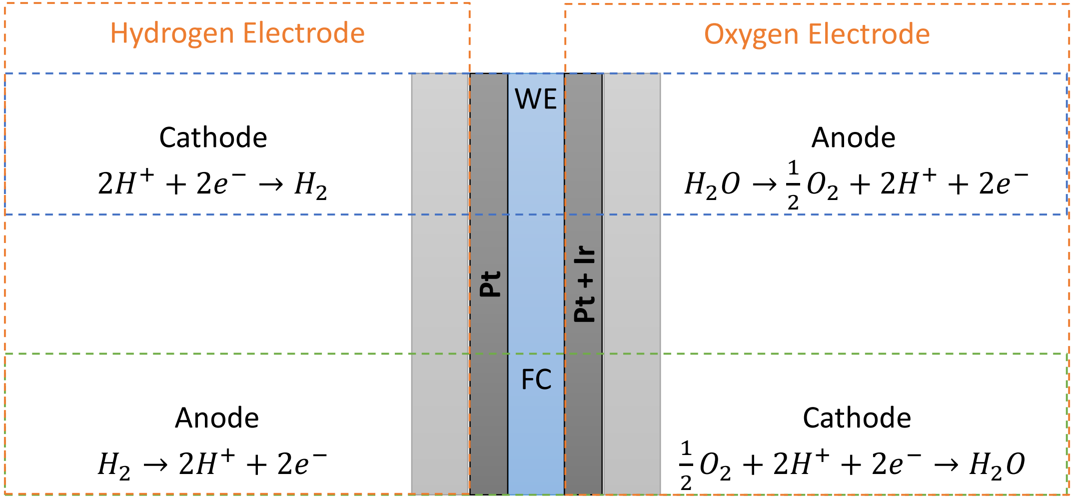
Redox-reaction-oriented desing

LOW TEMPERATURE PEM URFC – DESIGN

Gas-oriented design

Two fully reversible electrodes operate with the same gas during water splitting (charge) and hydrogen consumption (discharge): the hydrogen electrode carries out both the HER and the HOR while the oxygen one performs OER and ORR.

From the catalytic point of view, Pt is the most suitable catalyst for HER, HOR, and ORR. Conversely, Ir is needed to sustain the OER.



Hydrogen Electrode

Oxygen Electrode

WE

Cathode

$2H^+ + 2e^- \rightarrow H_2$

Anode

$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$

FC

Anode

$H_2 \rightarrow 2H^+ + 2e^-$

Cathode

$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$

This configuration requires fully reversible catalysts: both Ir and Pt have to be deposited onto the oxygen electrode.

Two layers of Pt and Ir can be deposited on the electrolyte or a Pt/Ir layer can be formed by coating a homogeneous mixture of Pt and IrO_2 nanoparticles.

LOW TEMPERATURE PEM URFC – DESIGN

The main problem in such architecture regards the GDL, more precisely it is related to carbon corrosion. In fact, at low electrode potentials (from 0.4 to 1.0 V), amorphous carbon is generally corroded via:

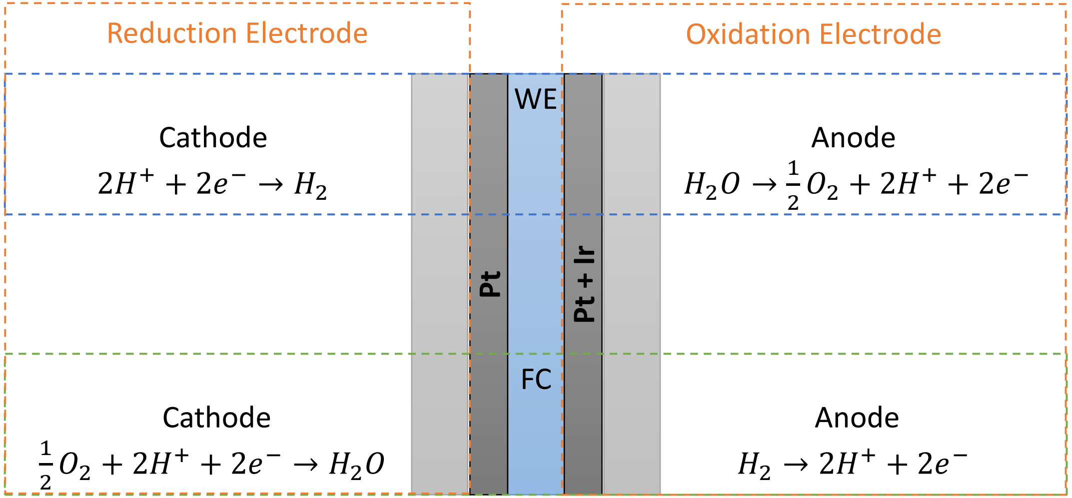
$$C + H_2O \rightarrow CO_2 + 4H^+ + 4e^- \qquad E = 0.206\,V$$

The rate of corrosion reaction get harsher and harsher as higher potentials are set, where also the graphitic domains start to degrade. While in fuel cell operation mode potentials larger than 1.0 V are reached only in some operating regimes (i.e. start-stop), while the URFC is run as an electrolyzer, the operating potential usually stets around 1.2 ÷ 1.3 V. In this regards, TiO_2 felts needs to be used.

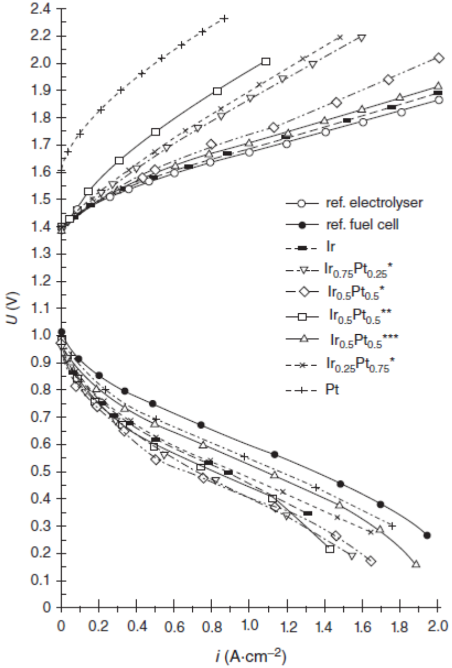
LOW TEMPERATURE PEM URFC – DESIGN

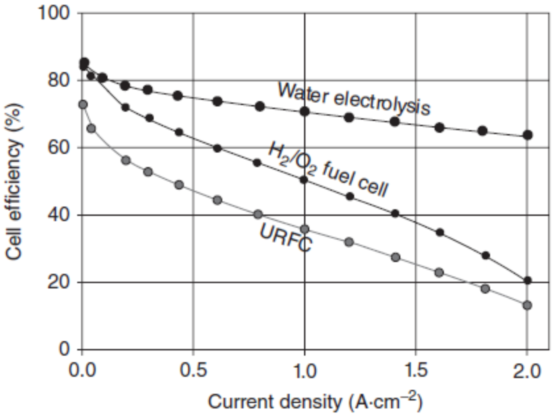
Redox-reaction-oriented design

The reduction electrode is carrying out both hydrogen (HER) and oxygen (ORR) reactions during WE and FC operation, while the oxidation electrode in parallel sustains both water (OER) and hydrogen (HOR). The main advantage consists in no need of carbon-made supporting material in the oxidation compartment. However, from an engineering point of view, complexity of the system increases. In fact, the system needs to be designed in order to allow gas circulation flows to be reversed, meaning that a full purge of cell compartments need to be performed to ensure safety. Moreover, electrode drying with an inert gas is needed when the device is switching form WE to FC operation mode (increase of standby time).



LOW TEMPERATURE PEM URFC – OPERATION





Research is still working for searching for catalysts formulations able to increase cells performances (overall at high current densities) and lifetime.

In some favourable cases, performances of the URFC can compete with best practices of individual PEM WE and FC, and the idea that a low-temperature URFC is a poor electrolyser and a poor fuel cell is therefore not exact.

LOW TEMPERATURE PEM URFC – SUMMARY

Performances and efficiency

When appropriate catalyst compositions are used, PEM URFC show comparable performances to conventional WE and FC (laboratory scale), and the global efficiency of a PEM URFC operating at 1 A cm^{-2} is about 35–40%. Performances could be increased by operating at higher pressures by external compression would be required (thus affecting system efficiency).

Advantages

URFC systems effectively are analogous to batteries which size is dependent on the size of the reservoirs instead of the size of the device.

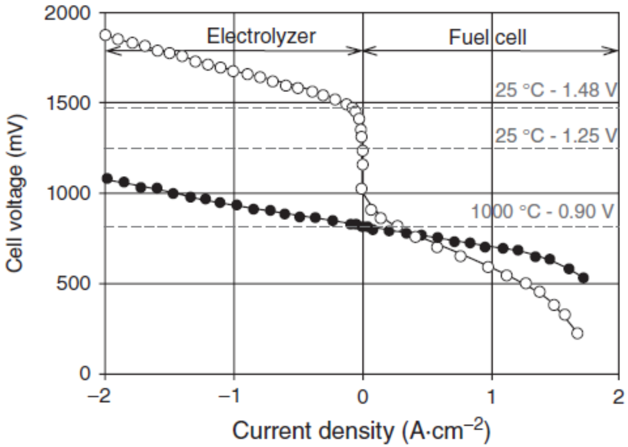
Drawbacks

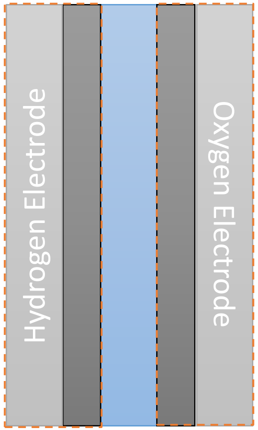
PEM technology uses expensive materials

Durability is constrained to durability of single FC and WE devices

HIGH TEMPERATURE PEM URFC

Based on solid-oxide technology operating ant high temperature, the main advantage relies in the fact that water/oxygen redox couple becomes fully reversible. Consequently, the gas-oriented design (characterized by lower system complexity) could be implemented.

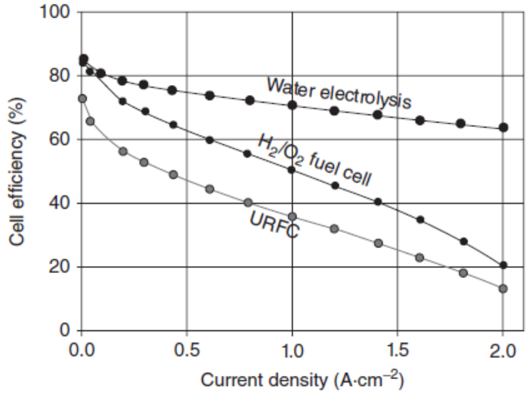




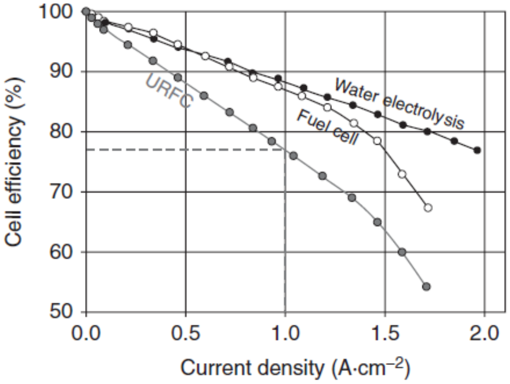
HIGH TEMPERATURE PEM URFC

Within such approach, the electrical efficiencies of both water electrolysis and fuel cell reaction are much higher than those obtained at low temperature using PEM technology because part (≈one-third) of the energy requirements can be supplied as heat. As a consequence, the electrical efficiency of the solid oxide URFC is significantly higher than the efficiency of the PEM URFC (≈ 78–80% at 1 A cm^{-2}).

Low-temperature URFC



High-temperature URFC



HIGH TEMPERATURE PEM URFC – SUMMARY

Advantages

Performances of solid oxide URFC are limited by those of solid oxide technologies, more specifically to the limitations connected to SOWE, having worse performance than SOFC. Overall, their efficiency is approximately twice that of PEM URFCs, about 75 – 80%.

Limitations

Durability is still and issue, as seen for SOWE for constant load operation.

UNIVERSITÀ
DEGLI STUDI
DI TRIESTE

Dipartimento di
Ingegneria
e Architettura