DREAMCAR Project

Direct Methanol Fuel Cell System for Car Applications

Introduction

The major benefit of the project is the demonstration of processes for **Energy production from a renewable energy source** with high overall efficiency and near to zero emissions to the environment. The proposed processes for electricity production from methanol via fuel cells offer a significant contribution to the Programme and the key action objectives: the fact that minimal production of CO_2 is taking place and no other pollutants (CO, NOx, HC, SOx) are emitted.

The benefits may be summarised as follows:

- **Greater dispersion of energy resources:** the gasoline-powered automobile will be with us for decades. The energy-importing countries of the world will benefit because there will be a larger number of suppliers of transportation fuels, and less energy will be required due to higher vehicle efficiencies.
- **Stable energy pricing:** price-regulating entities will find it increasingly difficult to control prices as the number of energy producers increases.
- **Fewer strategic crises:** the more production there is, the less chance there is that "tight markets" will turn a local crisis in one country into an international energy shortage.
- **Greater capacity for domestic self-reliance:** the development of renewable methanol feedstocks will offer many countries far more opportunities for self-reliance than can be discerned from current maps of the geographic distribution of natural gas resources.

Objectives and Targets

The primary purpose of the project is to develop **a complete Direct Methanol Fuel Cell** (DMFC) System for production of electric power. The main objective of the project was to design, manufacture and test a 5kW stack at high temperature (up to 140°C) passing via the intermediate objective of the design, construction and test of a 1.25 kW module.

There were three main axes of research:

• **higher operating temperature** (up to 140°C, depending on the membrane) to enhance the electrochemical reaction,

• development of **new fluorinated** (improvement of the membranes developed in the frame of the NEMECEL JOE3-CT-0063 Contract) **and hybrid inorganic-organic membranes**,

• development of **new carbon supported Pt-alloy catalysts** to increase the efficiency of the electrodes and power density.

The **specific scientific and technological objectives** of the project were :

- to develop membranes, catalysts, electrodes
- to define MEA preparation methods
- to choose the best performing MEA
- to manufacture and test a single cell
- to design and manufacture a 1.25 kW module
- to test the 1.25 kW module
- to evaluate the 1.25 kW module testing result for the optimisation of the components for a 5kW stack
- to design and manufacture the 5 kW stack
- to test the 5kW stack

The development of protocols and stack components (monopolar plates, bipolar plates, gaskets etc) have been carried out as well.

Parameter	*Objective*
Fuel cell operating mode	Direct Methanol Fuel Cell (without reforming)
Operating temperature	130 – 140 °C
Fuel	Methanol/water mixture
Oxidant	Air
Maximum noble metal loading	1 mg/cm²
Power density	300 mW/cm²
Minimum specific power	100 W/l and 80 W/kg
Optimum specific power	250 W/l and 200 W/kg
Stack power	5 kW

Consortium

In order to reach successfully all the targets of the project, the partnership included one car manufacturer (**CRF**, Italy) for the specification transfer, life cycle analysis and final testing, one engineering company (**THALES Engineering & Consulting**, France) specialised in the field of electrochemistry and project management, one company (**SOLVAY**, Belgium) experienced in the manufacturing of polymer membranes, two research institutes (**TAU RAMOT**, Israel and **CNR-ITAE**, Italy) skilled respectively in electrocatalysts and membrane development including scaling-up of material production and MEA large-scale preparation.

Scientific and technical description of the results

Different types of membrane were tested in order to achieve optimum technical performances at the operating conditions. Partners worked to improve **radio-chemically grafted membrane** (obtained during the NEMECEL project) as well as to modify polymers by **sulfonation** and to develop and characterise **NP-PCM** (nanoporous proton conducting membrane) and **SASA** (Silica anchored sulfonic acid) membranes. Demonstrated the improvement made of 5cm^2 **NP-PCM** based DMFC over the years up to maximum power density of 500 mW cm^{-2} for second-generation NP-PCM based DMFC. It was achieved in a combination of a commercial cathode, a homemade anode and a second-generation NP-PCM, at 130°C under dry air feed. This is 67% over the project target of 300 mW cm^{-2} at 140°C.
Despite excellent results, it was decided not to use this type of membrane since it requires an acidic electrolyte to make the membrane conductive. This is incompatible with the materials envisaged for use in the construction and test of the stack (severe problems of corrosion and fluid management for industrial application).

Development work on the **chemically grafted membranes** did not give the hoped results. It was found difficult to obtain a good combination of conductivity, insolubility in water/methanol mixture and good casting ability. The acquisition by SOLVAY of a new company offered new possibilities, in particular a new fluorinated polymer membrane called Hyflon Ion. This first sample gave excellent results with a power of 210 mW/cm² at 130°C with air feed and when assembled into an MEA with E-Tech electrodes at 2 mg.cm² metal loading. As this first sample, before any optimization, was giving good results, a new evaluation using the CNR catalyst was conducted and allowed to reach 255 mW/cm² at 130°C under air feed, that is to say the mid-term objectives of the contract. The work done later was focused on the optimisation of such membrane in terms of methanol crossover, hydration, resistance.

The selected membrane is called DREM04 and it was chosen at the 18th month meeting: in the single cell test with DREM04 - CNR catalysts, a power density of 287mW/cm^2 has been achieved.

Three different approaches have been pursued by the CNR-ITAE for the preparation of the anode catalyst. In the first approach, 85% Pt-Ru (1:1)/C bifunctional catalysts were prepared and optimised in terms of morphological and physico-chemical properties. Alternatively, in the second approach, Pt decorated unsupported Ru catalysts with a Pt concentration of only 2% were synthesised and electrochemically tested in DMFC. In the third approach, Pt-Ru-W supported on a carbon black catalysts were synthesised and investigated. Due to the slow methanol reaction kinetics it was necessary to use Pt loadings of 2 mg cm^{-2} with conventional catalysts, whereas the Pt loading was reduced to 0.1 mg cm^{-2} for the decorated catalyst. The catalysts were prepared in accordance with a specific procedure.

Test parameters for the comparison of membranes have been defined. A technology transfer between Partners was made for the preparation procedure of electrodes and Membrane and Electrodes Assemblies (MEAs). THALES, using the MEA preparation method developed by CNR, manufactured the first big MEAs (300 cm²). CNR manufactured the MEAs for the 1.25 kW module and 5 kW stack. A new MEA assembling procedure, developed by CNR, has been applied for the 5kW stack to avoid the need of a press with very large plates. A detailed description of the methods for methanol cross-over measurements was provided emphasising the use of the CO_2 detection method at the cathode for the determination of fuel efficiency.

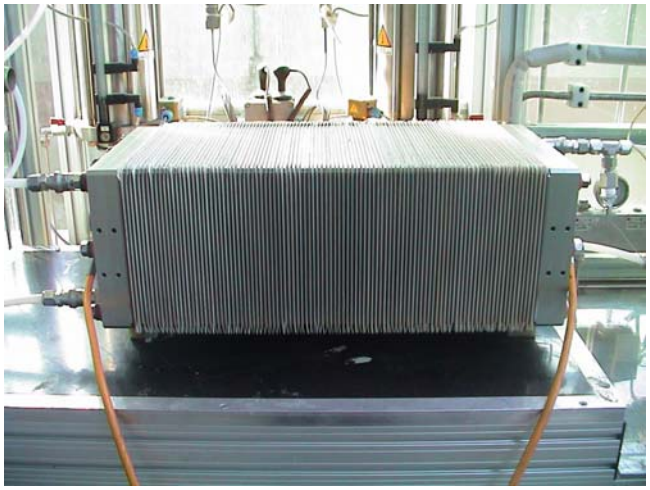
RAMOT carried out testing of its own membrane in a 5 cm² single cell and a 50 cm² small module. CNR tested the SOLVAY membranes associated with CNR electrodes in a 5 cm² single cell.
Using a 100 cm² single cell and a 300 cm² prototype cell that they designed and built, THALES realised the electrochemical characterisation of the selected materials developed by the partnership. The influence of temperature, pressure, gas composition and stoichiometry was evaluated. Final qualification of the MEAs was done with endurance tests.The 1.25 kW module, using composite graphite monopolar and bipolar plates, anodised aluminium clamping plates and silicon and EPDM gaskets, was designed, manufactured and tested up to 140°C by THALES. The 5 kW stack was designed and manufactured by THALES and tested by CRF. Some minor changes were incorporated into the 5 kW stack plate design, notably reshaped fluid inlets and outlets to provide the higher throughput of air and methanol mixture necessary to accommodate the increase in the planned cell number from 60 to 100.A customised fluid flow simulation computer programme was used to determine the optimum configuration. This major change, approved by all parties, was necessary to compensate the lower than anticipated power output of each cell in order to achieve the target stack performance of 5 kW. This substantial increase in the number of cells has of course a detrimental impact on the final specific power developed. The integrated simulation platform has been used for the definition of a control strategy for the methanol recycling device. The rapid prototyping of the control algorithms (defined in Matlab/Simulink environment) is performed using a dSPACE "MicroAutoBox" control unit which combines the characteristics of an automotive control unit with the flexibility of a rapid prototyping tool for control algorithm.
A Matlab/Simulink model and a functional model for the control system is implemented. A 'top-down' methodology has allowed the identification and the modeling of the basic components of the fuel cell system. The result is a hierarchical model made of independent subsystems which are logically interconnected. The single subsystems can be modelled independently form one another, and this makes it easy to analyse, debug, manage and upgrade the model.

The methanol recycling devices have been assembled in accordance to the testing specifications of the module and stack. The attention was focused not on the auxilliary systems integration but on the flexibility/functionability of the recycling devices in order to follow the test specifications for the module and stack tests.

The module and stack have been tested.

The module was operated under different conditions in terms of: methanol concentration, pressure, temperature, flow rates of both reactants, air humidification condition. The electrochemical investigation concerned internal resistance measurement, polarization measurement (module and individual cells).
The maximum power of the module is increased by approximately 20% by increasing the operating temperature from 80 °C to 130 °C. Methanol crossover seems to reduce the catalytic effect generally associated with an increase in temperature. The output power with oxygen was twice that with air but was still low.
The membrane and MEA manufacturing procedure improvements gave better results with less crossover. After this the MEAs for the stack were manufactured.

The following figure shows the 5 kW stack installed on the CRF test bench.



5kW Stack

Two set of experiments were carried out to test the 5kW stack. The overall stack voltage and each individual cell were monitored to record the open circuit voltage (OCV) performance and the polarisation curves under different current loads. The methanol concentration for the first set of tests was 1M and the for the second set was 0.5M. The very ambitious final stack performance target of 5 kW was almost achieved during the first set. Unfortunately only one set of tests was performed at 130°C. During the second set, internal damage, of unknown origin, occurred at 90°C and this affected the overall performance. It was not possible to go on with the experiments. It is evident that serious damage occurred to one cell and this influenced the nearby cells, which started to work in the reverse mode as well.

The following table provides a comparison of project objectives and results obtained.

Parameter	***Objective***	***Result***	***Comments***
Fuel cell operating mode	DMFC (no reforming)	√	
Operating temperature	130 – 140 °C	√	
Fuel	Methanol/water mixture	√	
Oxidant	Air	√	
Maximum noble metal loading	1 mg/cm²	2 mg/cm²	Loading necessary to achieve performance target in small cell
Average Power Density	300 mW/cm²	160 mW/cm²	Almost achieved in small cell but efficiency lost in scaling up to large cell
Minimum specific power	100 W/l and 80 W/kg	110 W/l	Volume and weight of stack increased following need for 100 cells instead of 60. Without this, figures would have been 200 W/l and 140 W/kg approximately
Optimum specific power	250 W/l and 200 W/kg	70 W/kg	
Stack power	5 kW	4.9 kW	

An essential Cost Analysis has been realised considering the main components of the 5kW stack and their assembly phase, described as follows:

1. Membrane (for 5 kW)
2. Electrodes:
    - *Ionomer (Nafion solution)*
    - *Catalysts (Pt, Ru, Carbon black)*
    - *Supports (carbon cloth)*
3. Monopolar and bipolar plates (moulded composite graphite)
4. Gaskets
5. Metallic housing and manifolds (anodised aluminium)
6. Assembly activities

During the next 5 years it could be possible to have a cost reduction of one order, if a wide scale production would be started: therefore the cost could get to about 300 €/kW.

Assessment

The project confirmed the validity of the principle of a direct methanol fuel cell working at high temperature to enhance the electrochemical reaction.

The very ambitious performance targets in terms of specific power and catalyst load targets were not completely achieved for the stack. As is often the case, the very good results obtained during small scale laboratory experiments were degraded subsequent to the scaling up to the industrial configuration of the stack. Nevertheless good progress was made in terms of membranes, catalysts, MEAs development and stack design and manufacture. Moreover the protocols that were defined represent a positive step forward in the field of Fuel Cell know-how and experience.

Due to the slow methanol reaction kinetics it was necessary to use electrodes with Pt loadings of 2 mg cm^{-2} with conventional catalysts. Alternatively, Pt decorated unsupported Ru catalysts with a Pt concentration of only 2% were synthesised and electrochemically tested in DMFC. Moreover Pt-Ru-W supported on a carbon black catalysts were synthesised and investigated.
The decoration approach appears to be quite promising for the reduction of the noble metal loadings and further optimisation may provide the breakthrough to promote the commercial application of these devices in combination with a low cost polymer electrolyte membrane.

Technical highlights/lowlights

- The targets of power density and operating temperature were achieved at the single cell test level, the new catalysts and the new membrane have better performances in comparison with commercial materials.
- The catalyst production procedure was scaled up to produce the quantity of catalyst needed for the 1.25/5kW module/stack.
- The module and stack were assembled with the produced MEAs.The observed variations in the performance of the MEAs, made individually by hand in the laboratory, need to be minimised. The problem should disappear in series production. Both the module and the stack worked, but at lower power densities than the single cell (same type of MEA) possibly due to some methanol passing through the large membrane ("crossover"). The final stack performance target of 5 kW, again very ambitious, was almost achieved.
- The dSpace hardware is suitable for the control of the methanol recycling device. It was applied to control the electrical heater, pumps, sensors and monitor the performances. A specific software developed in-house has been used.
- Necessity to optimise the heat integration, a lot of heat/energy is required to operate at 130/140°C at 3-4 bar.
- High air flow, due to the high stoichiometry, and high pressure needed to improve the efficiency of the electrochemical reactions.