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BZ-BattExt – DMFC as Battery-Extender in solar-boat application

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Abstract

For special applications Direct Methanol Fuel Cells (DMFC) are close to commercial application or already commercialized today. However for the step from laboratory to a broader market of fuel cells, a significant cost reduction, as well as an improvement in life time and power density of the systems is needed. These items were the focus of the project BZ-BattExt, to be reached by new knowledge in alternative materials, operation strategies as also the realization of enhanced sub systems. In the project a 100W DMFC compact system as battery extender was successfully developed and operated. The reduction of the number of components and the simplification of the system leads to a reduction of price, weight and volume. The project was funded by the German Federal Ministry of Education and Research in the program of Micro fuel cells. In the project the feasibility of a micro-DMFC system was evaluated which enables a minimized system periphery due to an improved system architecture. For this, alternative materials and functional components were developed and investigated. New membranes with reduced water and methanol permeation allow operation at low air stoichiometry and favorable system efficiency. Gas diffusion layers of various compositions were tested and optimized material was selected. New sealing materials with good methanol stability and optimized process ability in commercial production process were developed. MEA preparation was adapted to the new materials. The use of a simple, cost-effective way of stack production was demonstrated for DMFC use. The investigation and construction of enhanced subsystems and operation strategies, which enable and optimize the use of new components and materials, as also the realization of the micro-DMFC system were focus of the project. The technical feasibility of the results was investigated in the application, which means it was tested as battery extender of a solar boat. The DMFC fuel cell system serves as a basis for an efficient, compact and cost effective alternative for battery- or battery-extender systems and can fulfill a broad variety of applications.

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Introduction

DMFC technology, using methanol derived from biomass or other renewable energy sources, gives the same advantages as PEMFC technology, e.g. high energy efficiency, low or zero emissions. However DMFC technology has a number of additional advantages over PEMFCs: it does not have hydrogen storage problem; its delivery infrastructure is cheaper than for hydrogen; and emissions are significantly lower than for petrol- or diesel-fuelled generators. Eliminating the need for a reformer also facilitates technical simplification, and thereby reduces the size and weight of portable or mobile power-generator systems. The major stumbling-block for the further development of DMFC technology is methanol permeation through the polymer electrolyte membrane, resulting in fuel loss, lower cell voltage and release of methanol to the surrounding. But also the water diffusion leads to decreased power density caused by diffusion limitations for Oxygen. Additionally to that there is also apart from the performance the high cost of the state-of-the-art membrane. This has led to much intense research in recent years aimed at developing new polymer electrolyte materials with minimized methanol cross-over. Other major on-going research activities address the development of alternative catalyst materials or reducing the needed amount for both the fuel- and air electrode. The low emission characteristic of DMFC power supplies also facilitates application in new areas like recreational, indoor and low-noise applications.

1. Scientific Approach

The target of the project is to realize a cost reduction and enhancing the lifetime as also improving the power density of Micro-DMFC-Systems. For this a 100W DMFC System was developed by research and development of alternative materials like membranes, sealing's and MEA materials. One focus was to optimise the materials for operation temperature below 50°C which enables a favourable system design. A further goal in the membrane development [1-3], was a non expensive material with reduced methanol crossover and water diffusion [5-6]. The goal in the MEA development was a high power density at moderate temperatures and low catalyst loadings. The operation strategies as also the subsystems are developed in respect to realize a system with a minimised system periphery and by using commercial available components. The stacks for the system were developed within this project and comprise an enhanced sealing technology. The system was integrated in a solar boat as battery extender.

2. Experiments

Membrane development:

Within the project new materials for non- or partially fluorinated sulfonated block-co-polymer blend membranes were developed. The Phase-separation of block-co-polymers into hydrophilic and hydrophobic domains (see fig. 1) increases the proton conductivity and reduces the methanol permeability. However, the non crosslinked multiblock-co-ionomers shows a high degree of swelling and therefore a poor mechanical stability.

Due to an ionic-crosslinking (see fig. 2) of acidic block-co-polymers with basic polybenzimidazole (PBIOO®) the phase-separated morphology can be stabilized and ensures a stable membrane performance.

The new materials show comparable performance to Nafion and reduced methanol permeation. Furthermore the water permeation was reduced and the cells can be run at lower air stoichiometry or higher methanol concentration. The new materials can be a cost-efficient alternative to Nafion.

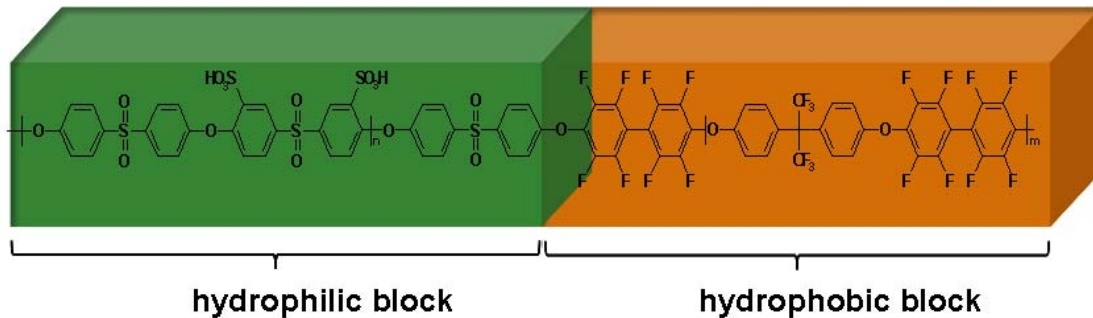


Fig. 1: non-or partially fluorinated sulfonated block-co-polymers

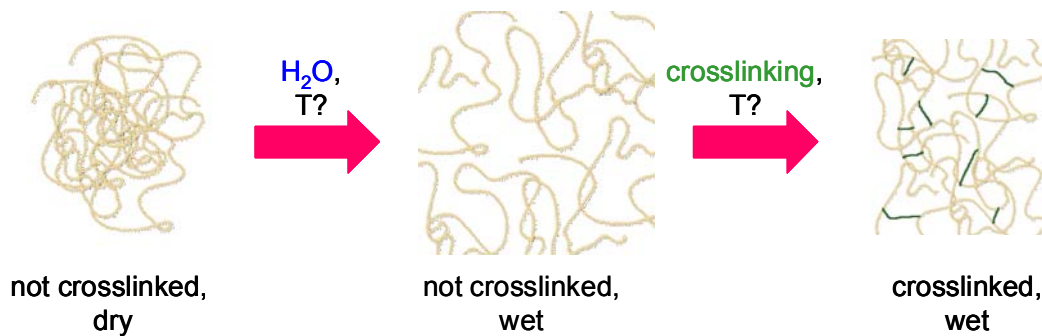


Fig. 2: concept of ionic cross-linking

MEA preparation and testing:

The dry spraying MEA preparation technique developed at DLR [4] was used to prepare MEAs with commercial as well as project membranes and GDLs using a test cell as developed for the project stack. The effect of variation of GDL parameters, reaction layer ionomer content, catalyst loading and membrane properties on the behaviour of the DMFC was investigated with the purpose to get a high power density at low temperature (50°C to below 70°C), low air stoichiometry at ambient pressure and low catalyst loading.

Optimisation of the GDLs and the reaction layer composition allowed to reduce the cathode stoichiometry from 4 to 3 and the catalyst loading for anode and cathode in total from 3.6 mg/cm² to 2.4 mg/cm² retaining the cell power density in the same range. At 50°C and low air stoichiometry ($\lambda_{\text{air}}=4$) a power density of 50 mW/cm² was obtained, at 70°C and a low air stoichiometry ($\lambda_{\text{air}}=3$) a power density of 70 mW/cm² was obtained (see Fig. 3).

Commercially available GDL types of FCCT with a more open structure as well as a less open structure were tested for anode and cathode. It turned out that using the open structure GDL the power density at high air flow is higher, however using the less open structure GDL the air stoichiometry can be reduced with only a minor reduction in performance.

Using a new developed membrane of ICVT the same MEA preparation technique was applied and some parameter optimization performed. At the present status MEA power density with the new membrane comes close to that with Nafion, the long term stability is also comparable. Considering that the adaption of the MEA preparation parameters to the new membrane is not yet finalized the ICVT membrane PKK57 can be seen as a very promising alternative to Nafion.

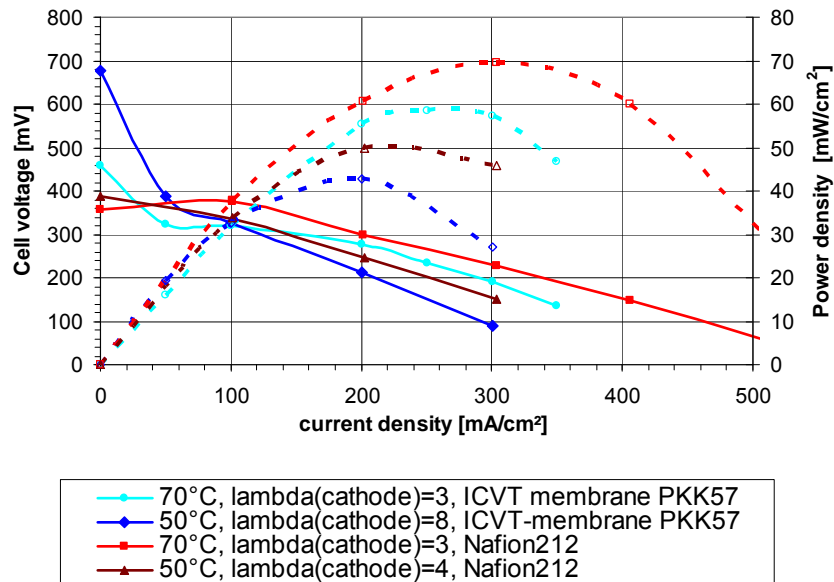


Fig. 3: Polarization curves of MEAs prepared with DLR dry spraying technique with Nafion respectively ICVT membrane. Total catalyst loading 2.4 mg/cm². 2M methanol solution, air, ambient pressure, reaction layer: Pt-/PtRu-Mohr with 60% Nafion, anode and cathode less open GDL by FCCT

3. Results

Stack sealing development

To meet market requirements for fuel cell series production, integrated profiled seals are necessary. The process of seal integration has to be adapted to mechanical sensitive stack components like graphitic bipolar plates and soft goods (membranes, GDLs or complete MEAs). Therefore low viscous elastomer materials are needed.

Up to now, silicone fulfills these requirements with regard to processability and mechanical properties. But nearly all available silicones provide insufficient chemical resistance in humid and acidic media.

Within the project, Freudenberg FCCT has developed a new stack sealing material on a polyolefin basis (2-component recipe) with improved stability in the DMFC environment. It is suitable to withstand the aggressive media in the DMFC environment and due to a low viscosity can be integrated on mechanically sensitive components like gas diffusion layers.

It has been demonstrated that the production of this material is reproducible and that it is process able using an injection moulding process.

A scale up from the laboratory scale to a pilot plant scale (20l) was made and an optimization of the mixing time (~35%) was reached. A direct integration of the seal onto the GDL according to the "FAST" concept (2 sealed GDLs connected by film hinge) was realized.



Fig. 4a: Pilot plant for sealing material

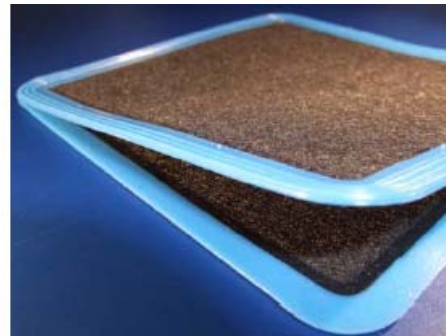


Fig 4b: FAST GDL concept

A stack sealing design for a conventional type stack was developed. An integrated sealing on the project GDL was realized using cold runner technology. For this an in-mould assembly (cold runner mould with needle valve nozzle) was built up. Product samples for stack manufacturing were fabricated. This „Fast GDL“ concept allows a simplified cell assembling.



Fig. 4c/d: stack sealing design for FAST GDL sealing and in-mould assembly



Test stack development

By merging the results of MEA, sealing and flow field development, a stack concept capable for FAST GDL and project flow field was developed. The construction of bipolar plates and stack components were made and the assembling of the test stack was completed by integration of the project MEA and FAST GDL sealing.

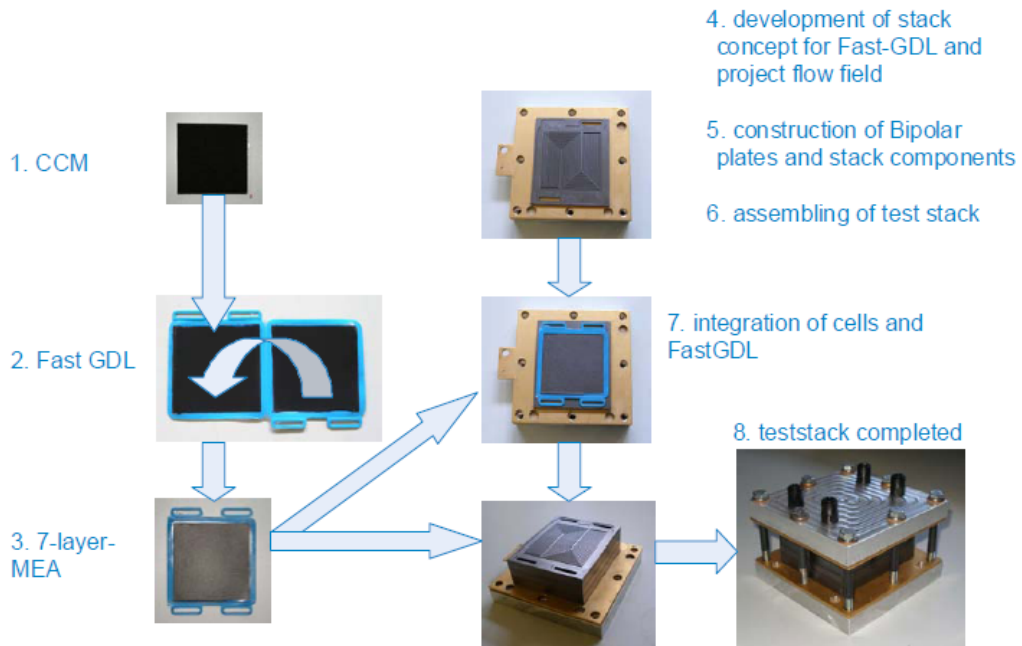


Fig. 5: Assembling of test stack with integrated sealing

Lamination sealing concept

As an alternative sealing concept the lamination and sealing of the cells by using synthetic resin, which is already available in PEM-technology, was transferred to the DMFC-technology.

New flow field designs for DMFC-Application were developed in respect to the existing stack design of a commercial available PEM-stack with this sealing technology. Short-and full stacks were developed by this “rapid prototyping” and cost efficient technology. The stacks were built up and characterized with commercial available MEAs and project MEAs integrated.

The DMFC-stack development by using this sealing technology was successful and was demonstrated with a 30W and a 120W stack. An extension of the cell numbers to reach a stack power of 150-200W is feasible.



Fig. 6: short and full stack with lamination sealing concept

The stack parameters of the full stack are:

- power 120W
- weight 2096g
- size 19 x13 x5,5cm
- commercial stack concept (Schunk, PEM)
- small scale series production plant available

The stacks were characterized according to power as function of operating conditions (temperature, pressure, fuel flows etc.) as also to the new flow fields and sealing technology.

The stacks shows high performance, good reproducibility and a low pressure drop. The goal of a high power density at low operation temperature and pressure was reached.

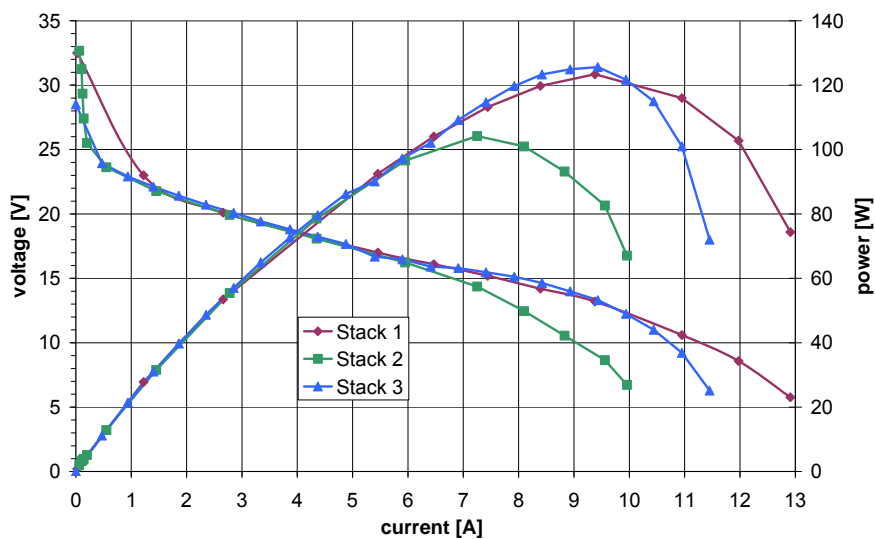


Fig. 7: polarisation curves of full stacks

System development

For the design of the DMFC system subsystems for the methanol and water supply, the air supply, heat management and concentration control has been developed and investigated. The choice of components has been done in respect to use commercial available components with low costs and little power demand. Operating procedures and control strategies has been developed and tested. The system architecture is made in respect to a stable operation and to realize the system with a low number of components.

A 100W demonstrator system was developed and built up as a compact stand alone system. The sensorik of the system has been reduced to 3 Sensors. A sensor free methanol-concentration control was realized. The number of active components was reduced to 4, the water recovery from the cathode exit was realized without active cooling. The construction of the system was made on a base plate, which can be integrated in a PC-enclosure.



Fig. 8: DMFC portable stand alone system with open case and in PC enclosure

The system specifications are given as follows:

system:	DMFC
power:	100 W _{nom.} (120 W _{stack})
cooling:	none (case cooling)
weight:	13 kg
weight DMFC-system:	7,5 kg
weight of case:	5,5 kg
size (l x w x h):	49 x 21 x 50 cm
MeOH-consumption:	ca. 1,50 ml/min (0,9 l/kWh)
power density:	320-475 Wh/kg (5 l tank)
capacity:	55 hr full power (5 l MeOH)
power demand BoP:	15-25 W (12-19%)
power electronic:	10-20 W (8-16%)
efficiency	ca. 25%

Boat integration

The DMFC System is used as battery extender for a solar boat. The Fuel cell is coupled with the accumulator of the boat by a solar-charge-controller and in parallel to a solar module. The Fuel cell will be operated at maximum nominal power. The power for start up of the Fuel cell is taken out of the accumulator. The accumulator can be charged by the fuel cell. .

By integration of the Fuel cell an increase of the cruising range and the time of operation can be reached of approx. 30 %.

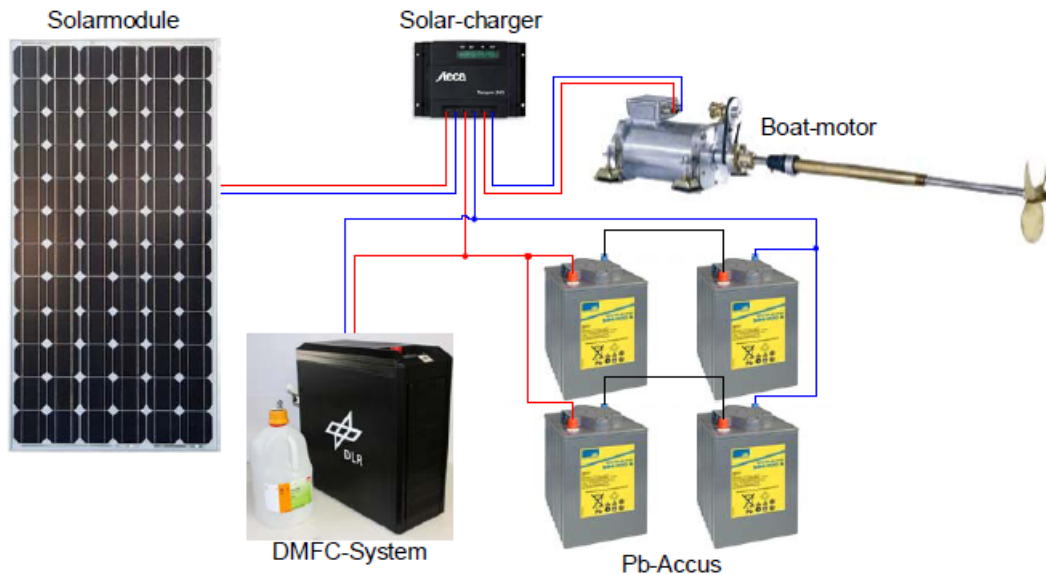


Fig. 9: Hybrid concept of the DMFC-System as battery extender

For the integration of the DMFC system into the boat, a restyling of the boat-hull was made under hydrodynamic aspects and for an upgrade for 6-8 people. Furthermore, the boat design was modified for a simple installation of the solar module. Stability calculation was done and verified from accredited laboratory. The Fuel cell was integrated into the helm stand of the solar boat to have a good accessibility and connection to the power electronics of the boat.

The Fuel cell system was successfully integrated and tested during boat operation on the lake constance.



Figure 10: solar boat SOL20 with DMFC-system

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