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Coating of reaction layers with a spraying process for fuel cell electrode applications

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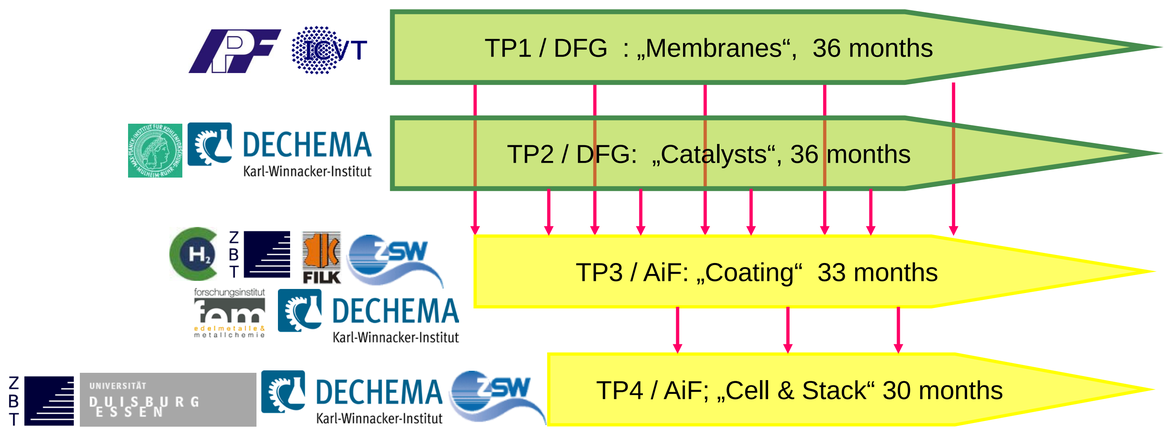
Introduction & motivation

Fuel cells are usually classified into working temperature categories. High temperature fuel cells (HTFC), such as the Solid Oxide Fuel Cell (SOFC) or the Molten Carbonate Fuel Cell (MCFC) are working in a temperature range of 600-950°C that allows a sufficient conductivity of the electrolyte. State of the art HTFCs have already shown high cell efficiency up to 60%. Low temperature fuel cells (LTFC) are mostly equipped with a polymer membrane such as Nafion whose conductivity depends on the presence of water molecules. Therefore, their working temperatures are usually limited to 80-90°C. With exception of MCFC that is specially designed for stationary electricity plans, both, high and low temperature fuel cells are planned to be used in a foreseeable future as energy converter for stationary and automotive applications. In the case of the LTFC, however, more robust systems and especially, more stable polymer membranes than PBI-based ones, which are still sensitive to cold starting processes that are able to work at 100-150°C are needed. Higher working temperatures mean higher efficiency of the catalysts, lower electrolyte resistances and as a consequence higher cell performances. These depend not only on the working temperature, kind of catalyst and membrane, but also on the purity of the fuel and its distribution within the diffusion and reaction layers and also on the evacuation of the reaction products, which can lead to catalyst poisoning and electrode flooding, respectively. The latter depends on the morphology and properties inherent to the diffusion and reaction layers, such as catalyst loading, porosity, hydrophobicity, thickness and additionally on the compression forces within the stack. For theses reasons, the design of the membrane-electrodes assembly (MEA) remains a very important step within the fuel cell concept. One distinguishes two strategies: the most common one consists on coating the electrodes with the diffusion and reaction layers (CCE) and finally press them together to a MEA. The second one aims to directly coat the membrane with the reaction and diffusion layer inks or pastes (CCM). The choice of the coating technique depends among other things on the thickness of the different layers and of the kind of substrate. For thin layers like in the case of the H_2PEM anode, where usually 0.25 mg cm^{-2} Pt is used as standard catalyst loading, the screen printing method is preferred. The spraying technique is more suitable if numerous coating steps are desired for example to achieve a catalyst gradient across the reaction layer.

Cluster description & organization

Ten German research institutes with complementary competences are involved in this cluster project that aims at the development of a middle temperature polymer fuel cell (MT-PEMFC). The list of these institutes as well as the cluster structure are shown in figure 1. This cluster includes four subprojects (TP). The first one (TP1) aims at the development of novel polymer membranes that are able to work at 100-150°C. The second one (TP2) focuses on the preparation of more efficient carbon supported Pt and Pt bimetal catalysts for the oxygen reduction in the hydrogen (H_2-PEMFC) and methanol (DMFC) fuel cells (TP2 – see M. Sakthivel poster for details). Different coating techniques such as screen-printing, spraying, sputtering and galvanic deposition onto either the gas diffusion layer (GDL) or the membrane will be improved and compared with each others in TP3. The ultimate goal in TP4 is the construction of two stacks with working temperatures in the range of 100-150°C:
- a 300W_{el} H_2 stack with integrated innovative cooling and wetting systems
- a pressurized DMFC stack working with a liquid methanol supply and without any external cooling system.



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Forschungsinstitut für Edelmetalle und Metallchemie, Schwäbisch Gmünd (**FEM**)
Energietechnik, Universität Duisburg-Essen, Duisburg (**UDE**)

Figure 1: Organisation of the cluster with interconnection of the different TPs for material delivery timing and list of the involved institutes.

Objectives and tasks of KWI inTP3

In this project, gas diffusion electrodes will be prepared with a spraying method and tested under half-cell and fuel cell conditions, principally for DMFC applications. For this purpose, a special coating machine equipped with an ultrasonic spray forming head was purchased by the USI company (see figure 2). The coating device is provided with a 4 axes selective coating capacity, using servo motors, screw actuators and stepper motors.

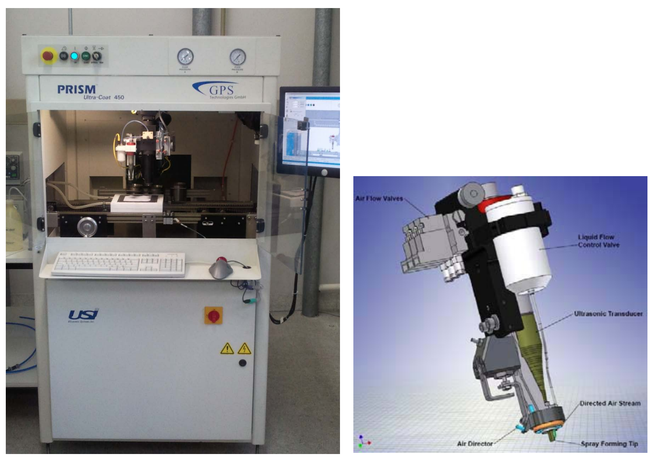

Fig. 2: Picture of the spray coating device Prism 450 (left) with spray forming head (right).

The main aim of this subproject is to develop a spray coating process, which performs homogeneous and well-defined porous layer structures of mono-dispersed electrochemical nanocatalysts. This process will be validated according scalability and reproducibility, and compared with other coating methods tested in TP3. The project tasks are described as following:

Task 1: GDL coating and determination of the spraying parameters

In the first step, a suspension made of carbon-supported catalyst, binding material (PTFE/Nafion) and solvent (H_2O and isopropanol mixture) will be prepared. The catalysts such as Pt- & PtRu-Vulcan for the anode and PtM-Vulcan (M=metal) for the cathode will be synthesized in TP2. Then, the coating parameters such as head distance and velocity, opening frequency of the ink valve have to be determined and optimized. To maintain an optimal three-phase boundary and contact with the polymer membrane (from TP1), Nafion will be substituted in the ink by a membrane alike ionomer.

Task 2: GDE characterization

The activity of the gas diffusion electrodes (GDEs) regarding hydrogen and methanol oxidation as well as oxygen reduction will be tested using an electrochemical half-cell in an ambient up to 50°C. Electrochemical impedance spectroscopy (EIS) will be performed in order to get some information about polarisation, contact and electrolyte resistances under half-cell and fuel cell conditions. CO-chemisorption, BET and SEM/EDX analysis will be performed to obtain information about active catalyst surface, pore structure and layer thickness, respectively.

Task 3 : Fabrication and characterization of MEAs

Hereby two coated GDLs will be stacked together with the membrane at a temperature between 100 °C and 150 °C to form a MEA. The most important challenge will consist on binding the partially- and non-fluorated membranes with the electrodes. Afterwards, in order to characterize the MEA's, U/I-, EIS and methanol permeation tests will be conducted in a 5 cm^2 single-cell DMFC.

Preliminary works and first coating tests

Fig. 3: Heating plate (left). ink reservoir (middle) and two carbon layers on a paper substrate (right)

To fulfil the requirements of the coating procedure that should be carried out at 60°C, a heater (fig. 3) made of a titanium metal case inserted in a Teflon jacket for better heat transport to the surface was constructed by our workshop. In order to maintain continuous drying rate of the solvent during the coating process and between two coating steps, hot water is pumped into the heating plate. Additionally, an ink reservoir made of glass that can resist to pressures up to 5 bar was constructed in a way that the suspension can be stirred by a magnetic stirrer to improve the dispersion ability of the ink. In order to determine the process parameters, such as head distance from the sample, head velocity, frequency of the opening valve for the ink supply, preliminary tests were conducted with a carbon Vulcan containing suspension without catalyst on a white paper substrate (see fig. 3).

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