INVESTIGATIONS ON SULPHUR IN A CATALYTIC CRACKER FOR PEM FUEL CELLS

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INTRODUCTION

Catalytic cracking is a promising route to produce hydrogen beside the well-known processes like steam or autothermal reforming. The catalytic cracking process is quite simple because the hydrocarbons are decomposited mainly into a hydrogen rich gas and solid carbon at elevated temperature with the aid of an appropriate catalyst. The carbon is deposited on the catalyst surface and has to be burned off in a following process step. Hence, for a continuous hydrogen production batch operation is necessary. The produced hydrogen-rich gas can be used in a fuel cell. A few prototypes of a catalytic cracker have been developed at the University of Duisburg in the last five years.

Liquid hydrocarbons for hydrogen production like gasoline or diesel offer a new way to a low cost and widespread fuel for different fuel cell applications. The main problem using these higher hydrocarbons as feedstock is the sulphur content. Sulphur can be present in the fuel in a variety of components, which are either converted to hydrogen sulphide (H_2S) in the cracking reactor during the cracking process or remain at the catalyst surface deactivating the catalyst. The converted H_2S can desorb from the surface of the catalyst and deposits partially on the subsequent methanisation catalyst, which thereby also is deactivated. Finally the remaining H_2S can reach the PEM fuel cell stack where sulphur components act as catalyst poison for the platinum anode catalyst (Fig. 1).

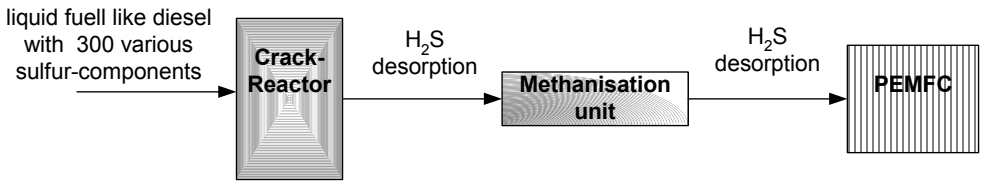


Figure 1: Simplified flow chart of a complete cracking system

In this context the sulphur tolerance of a PEM fuel cell is of great interest. In the following paper the results of an experimental investigation are presented, where hydrogen containing H_2S was fed to a membrane electrode assembly (MEA) in order to determine the sulphur tolerance.

EXPERIMENTAL

The University of Duisburg and the Zentrum für BrennstoffzellenTechnik GmbH use extensive analysis techniques for the detection of sulphur components at different concentrations (Fig. 2). The gas chromatograph is able to analyse various sulphur compounds in concentrations of at least 300 ppbv. The total sulphur analyser (TSA) is able to detect hydrogen sulphide in gases down to a level of 3 ppbv and hydrogen sulphide in sulphur containing liquids (e.g. diesel) in concentrations of more than 5 ppbw. For measuring the total sulphur content of a gas stream containing different sulphur compounds the TSA converts these substances into H_2S using hydrogen and synthetic air. This reaction takes place in a pyrolysis oven at a temperature level of 1250 °C.

Figure2: Sulphur analysis equipment (left: Total sulphur analyser, right: Gas chromatograph)

For the reduction of sulphur compounds in the feedstock various desulphurisation processes can be used. As these processes do not remove sulphur completely or a breakthrough shall be detected as early as possible a sophisticated analysis technique is necessary for the detection of the remaining sulphur content in the system. This is very important because the sulphur compounds shall not reach the PEMFC.

Former investigations into catalytic cracking of diesel with a sulphur content of about 0,2 wt.-% have shown that H_2S is produced by the noble metal catalyst during the cracking process. Figure 3 presents the measurement of the sulphur species of a cracking product gas with a gas chromatograph. It is obvious that all sulphur compounds have reacted to form H_2S because only the hydrogen sulphide peak can be detected.

Figure 3: Gas chromatogram showing H_2S formation during cracking of diesel (79 ppmv H_2S)

The experimental tests with regard to the MEA sulphur tolerance were performed using a small single cell PEMFC with an electrical power of about 10 W. The hydrogen fed to the fuel cell contained various amounts of H_2S (100, 50, 10, 5, 1 and 0,5 ppmv). During the test series commercial membrane-electrode-assemblies of the same manufacturer were employed. For each H_2S concentration three measurement series were performed in order to ensure the reproducibility of the measurements. The complete feedstock (a gas mixture of hydrogen and hydrogen sulphur) was fixed to a volume flow of 400 sccm. The purge rate of the fuel cell was set to 79 % to get defined conditions on the noble metal catalyst surface of the anode. The cell current was taken up at constant cell voltage of U = 0,6 V.

In order to achieve the optimum operating conditions the MEA was operated with pure hydrogen for 20 minutes before the gas mixture of hydrogen and H_2S was fed. Although the same membrane electrode assemblies were used and all test parameters were kept identically the measured current densities of each MEA were different at the beginning of the measurements. For the comparison of the test series the actual current density (cell run with gas mixture) was related to the current density of the fuel cell using pure hydrogen after 20 minutes. The relation j^* is given in percent and is drawn over the logarithmic investigation time (Fig. 4) and can be described as follows:

$$j^* = \frac{j_{(t)}}{j_{initial\ value\ t=20min}} \quad .$$

The current density $j_{(t)}$ depends on the time and is defined as the cell current $i_{(t)}$ related to the active cell area A:

$$j_{(t)} = \frac{i_{(t)}}{A}.$$

The curves in Figure 4 show that with increasing H_2S concentration the current density decreases faster. Even at very small hydrogen sulphur concentrations the cell power drops to a level of 10 % of the current density using pure hydrogen.

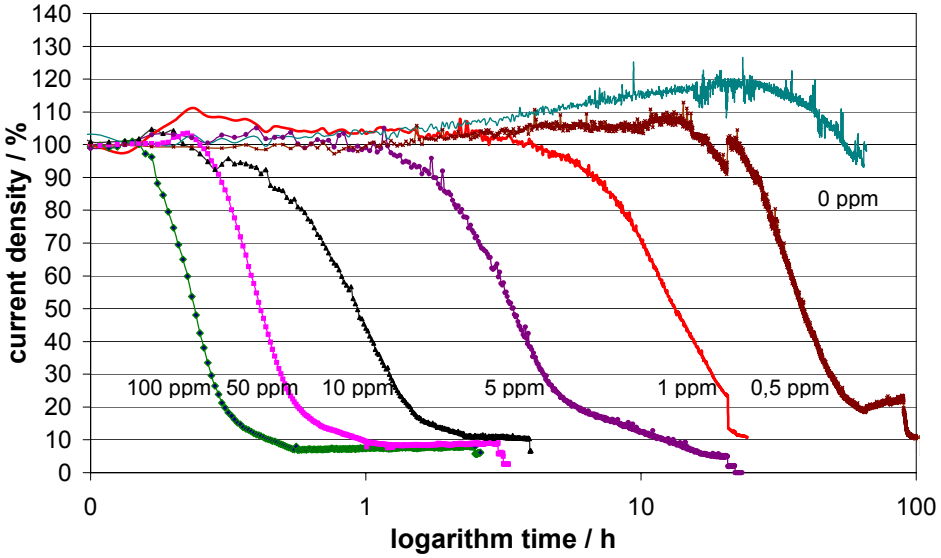


Figure 4: Current density curves of various test series (H_2S concentration in ppmv)

After reaching the power limit of 10 % the fuel cell was fed with pure hydrogen to investigate the reversibility of H_2S contamination of the MEA. Additionally load fluctuations and potential reversals were performed to reach this goal. None of these approaches were successful to achieve a regeneration of the MEA. The poisoning of the MEA is irreversible under these conditions, sulphur is probably chemically bound to the noble metal electrocatalyst.

In Figure 5 and 6 the current-voltage-curves at a hydrogen contamination with 10 and 0,5 ppmv H_2S are displayed after complete poisoning. Both diagrams show that the fuel cell behaves nearly the same. This is independent from the concentration of hydrogen sulphur in the fuel gas.

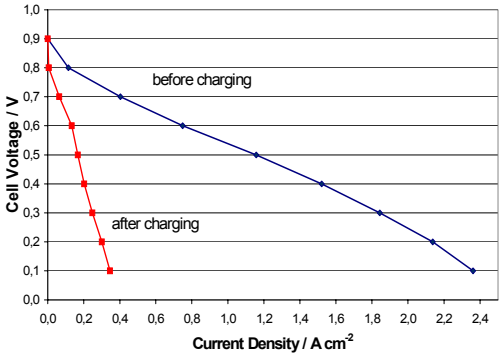


Figure 5: Current-Voltage-curve with no contamination and with 10 ppmv H_2S in hydrogen

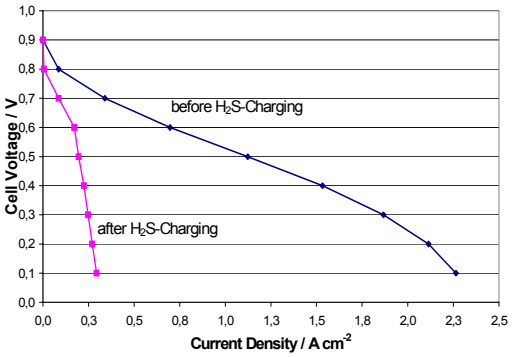
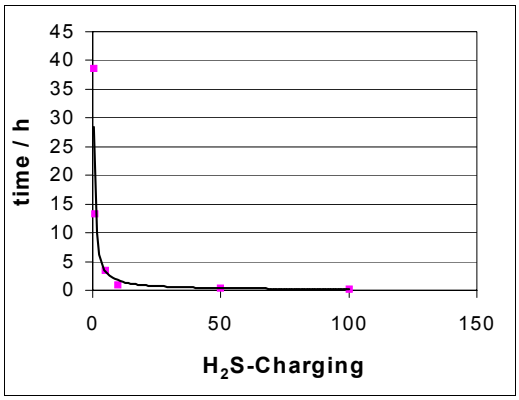


Figure 6: Current-Voltage-curve with no contamination and with 0,5 ppmv H_2S in hydrogen

The function displayed in Figure 7 shows the degradation time over the H_2S concentration at a degradation level of 70 %. This means that the fuel cell delivers a current density of 70 % related to the current density measured using pure hydrogen. The degradation time at any hydrogen sulphur concentration can be calculated as hyperbolic function described as follows:

$$t_{y(xH_2S)} = B_y \cdot \frac{1}{x_{(H_2S)}^{\gamma(x)}} .$$

B_y represents the degradation rate at given purge rate, $x(H_2S)$ is the H_2S concentration (ppmv) in hydrogen and $\gamma(x)$ is the exponential factor of the hydrogen sulphur concentration. These factors are given in the parameter table shown in Figure 7.



Degradationsgrad / %	By	γx
80	9.9832 xH_2S	0.9169
70	11.466 xH_2S	0.9273
60	13.193 xH_2S	0.9365
50	14.784 xH_2S	0.9441

Figure 7: Degradation curve of the fuel cell at a degradation rate of 70 % and parameter table for the calculation of the degradation time at any H_2S concentration given in ppmv

In Figure 8 the degradation times with appropriate deviation of the test series at different hydrogen sulphur concentrations are displayed. The diagram shows that at decreasing H_2S concentration in hydrogen the degradation time increases.

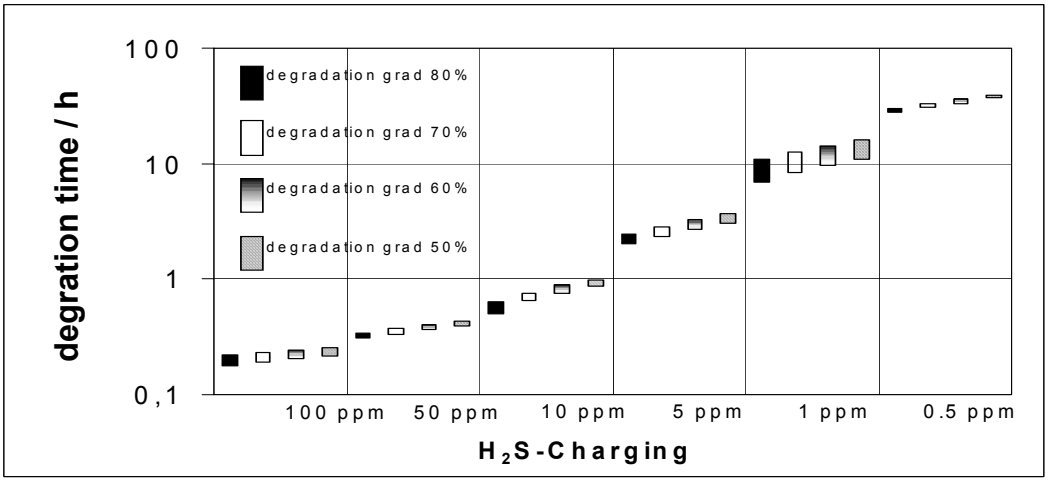


Figure 8: Degradation times including deviation of the test series

CONCLUSION

A single fuel cell with a commercial MEA was tested using different H_2S concentrations in the hydrogen feed. The results of the investigation show that the degradation of the fuel cell depends on the amount of hydrogen sulphur. Using the measured values a describing equation could be derived to determine the degradation time of the fuel cell at constant purge rate and at fixed cell voltage. The degradation time model is usable for degradation rates of 50, 60, 70 and 80 % of the start current density using pure hydrogen as feed.

REFERENCES

[1] T. Kalk, F. Mahlendorf, J. Roes,: „Cracking of Hydrocarbon to produce hydrogen for PEM Fuel Cells“, Fuel Cell Seminar 2000 Portland, Oregon