Fuel Cells

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November, 29th 2003

1 Introduction

In consideration of environmental problems and several energy crisis in the 20th century, much effort has been put into research on new energy sources as alternatives to fossile fuels. One promising approach is the controlled reaction of hydrogene and oxygene in a fuel cell. To create an electrical potential difference, the reduction and oxidation processes take place at two seperate electrodes. The process is catalysed by platinum.

In contrast to this simple chemical reaction, fuel cells have extremely complicated physical properties. In this document we will describe experiments on the physics of polymer electrolyte membrane (PEM) fuel cells. In this type of fuel cell the two electrodes are seperated by an organic membrane that is permeable for the H^+ ions coming from the anode, but not for the O^{2-} ions, H_2 and O_2 molecules. As this membrane only works properly if it is kept humid, the H_2 and O_2 gases are humidified so that they are saturated with water when entering the electrodes.

We will not go into further detail on the technical details of PEM fuels cells and instead refer to literature, especially to the script on fuel cells at

    http://www.physik.tu-muenchen.de/lehrstuehle/E19/fp57.html

2 Fuel cell thermodynamics

In this chapter we will deal with the dependance of fuel cell performance on temperature and gas pressure at the electrodes. To minimize dynamical effects, only the quiescent voltage U_0 is of interest here.

The central equation describing the thermodynamics of fuel cells is the Nernst equation

$$U_0 = U_0^0(T^0, p^0) - \frac{RT}{zF} \ln\left(\frac{p_{H_2O}}{p_{H_2} \cdot \sqrt{p_{O_2}}}\right) \tag{1}$$

In this formula $U_0^0(T^0, p^0)$ is the quiescent voltage of a fuel cell under standard conditions (1013 mbar, 298 K). Its value is 1.229 V. R is the common gas constant, T is the temperature in Kelvin, F is the Faraday constant and z is the number of electrons each H_2 molecule provides (i.e. 2). The argument of the logarithm consists of the activities of all substances relevant to the reaction. As all reactions in a fuel cell take place in the gas physe, these activities are equal to the partial pressures in bar. In our case the Nernst equation can be simplified a bit by assuming the activity of water is 1. This is possible because the cell is kept so humid that the activity of water does not change dramatically for different temperatues or gas pressures. The simplified equation is

$$U_0 = U_0^0(T^0, p^0) + \frac{RT}{zF} \ln\left(p_{H_2} \cdot \sqrt{p_{O_2}}\right) \tag{2}$$

2.1 Temperature effects

The black curve in Figure 1 shows experimental data for the temperature dependance of U_0 at gas pressures of 1 bar. The cathode gas was not pure oxygene but simply air. The red curve shows the corresponding theoretical values. They were calculated according to equation (2). The only problem that occurs when applying this
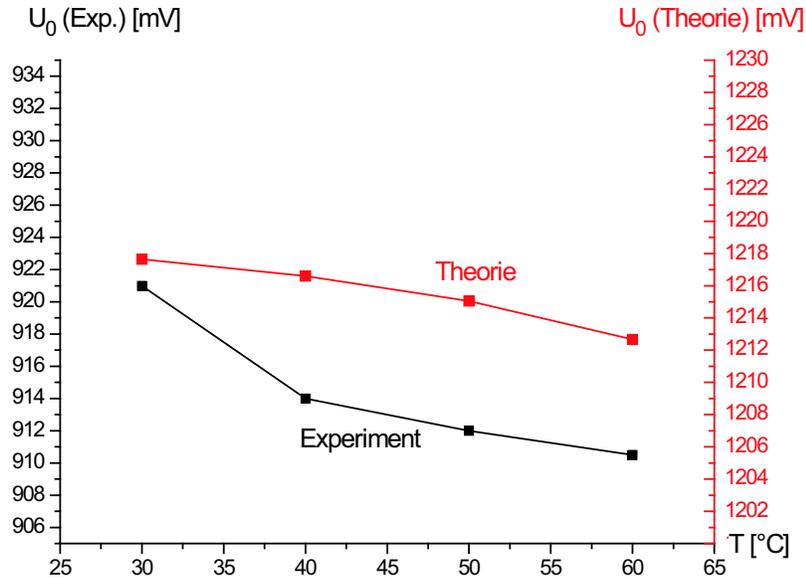
Figure 1: Experimental and theoretical temperature dependance of the quiescent voltage at a pressure of 1 bar. The cathode gas was air. Note that the axes for the theoretical value has the same scaling as that for the experimental data, but is shifted upwards a lot.

equation is the calculation of the gas partial pressures. As the gases were saturated with H_2O, the tabulated temperature dependant steam pressure of water has to be subtracted from the actual gas pressure. For O_2, the result still has to be multiplied with a factor of 0.20 because the air that was used as the cathode gas contains only about 20% of oxygene.

When comparing theoretical and experimental data the most important observation is a difference of about 300 mV (30%!)between the two curves. As the statistical fluctuations of the measurements was only around 2 mV this clearly shows that equation (2) does not describe all effects that appear in real fuel cells. In particular the limited reaction speed causes an overvoltage at the electrodes that is relevant even for very small currents as they occur when measuring quiescent voltages.

However the slopes of the theoretical and experimental curves are in quite good agreement, at least for temperatures above 40°C. As the measurement at 30°C was the very first measurement after turning on the fuel cell, the setup might not yet have reached equilibrium conditions here.

2.2 Pressure dependance of the quiescent voltage

Equation (2) predicts that besides temperature, gas pressures should also have a great influence on the quiescent voltage of a fuel cell. Figure 2 shows calculated quiescent voltages for several temperatures and for oxygene and air as cathode gas. In comparison to this theoretical data, figure 3 shows the actual experimental results for these conditions. Note that the scaling of the vertical axes is different for the two figures.

First we must note that there is again a large, but relatively constant difference between the absolute values, while the slopes of the curves match roughly: For higher pressures, the cell voltage increases logarithmically.

As one would expect, using pure oxygene instead of air increases the performance of the cell because the partial pressure of O_2 is increased this way. However the experiment shows that this effect is about twice as strong as theory predicts. This indicates that the overvoltages that cause the general deviation between the two curves depend on partial pressure.

The most tricky topic here is the temperature dependance: According to equation (2) the cell voltage should decrease as T grows for low pressures because in this regime, the ln-function is negative, while for high pressures,
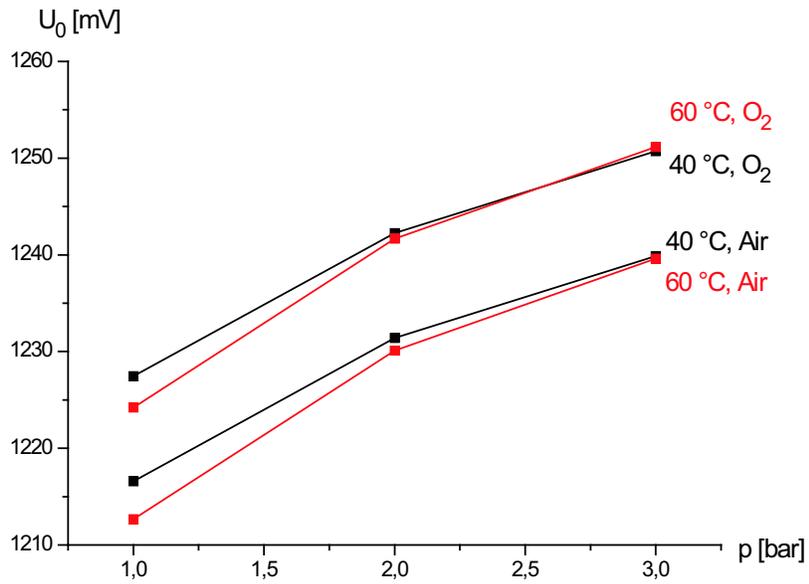
Figure 2: Theoretical predictions for the pressure dependance of the quiescent voltage for different temperatures and cathode gases
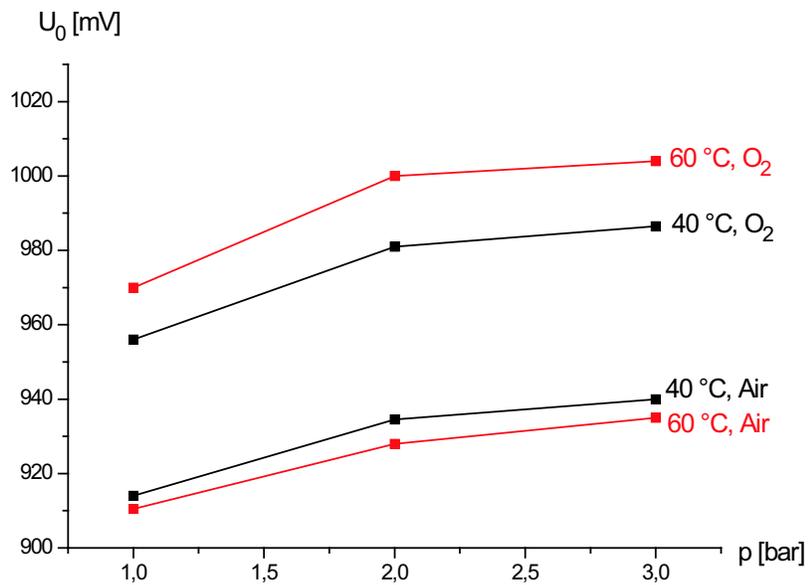

Figure 3: Experimental data for the pressure dependance of the quiescent voltage for different temperatures and cathode gases. Note that the scaling is different from that in figure 2
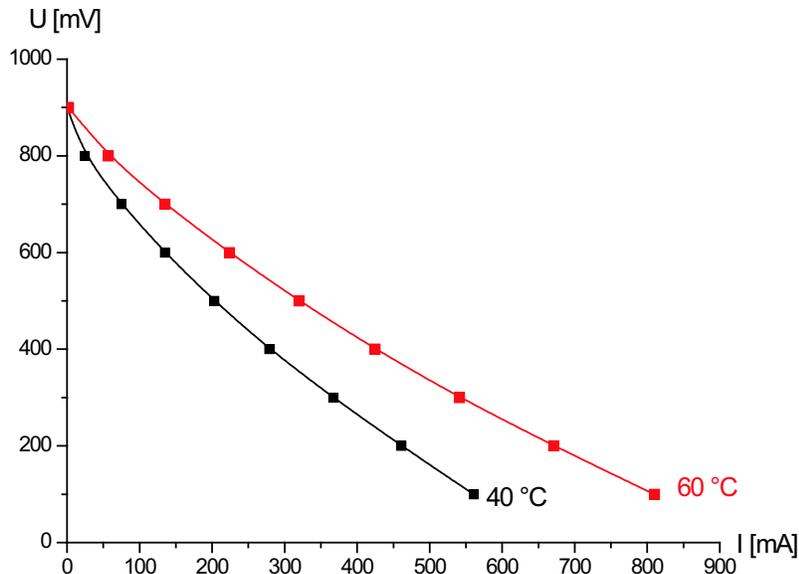
Figure 4: Current-Voltage curves of a loaded fuel cell for different temperatures. The pressure was 3 bar, pure oxygene was used as the cathode gas

U_0 should increase with T. However for higher temperatures the gases contain more water so the partial pressure that goes into the Nernst equation is again reduced. Therefore, the theoretical U_0 in figure 2 drops with increasing T except for the highest point at 3 bar and using pure oxygene.

In the experiment however, this phenomenon is much more significant: When using pure oxygene, the whole curve at 60°C is above that for 40°C. This shows that some of our assumptions were incorrect: First, the gases are probably not completely saturated with water because they pass the humidifyers at a finite speed. Therefore, the partial pressures of oxygen and hydrogene were higher than expected. Besides that, setting the activity of H_2O equal to 1 is probably not correct. If it was less than 1, we see from equation (1) that the transition between positive and negative temperature response will occur at lower pressures.

3 Fuel cell kinetics

Although the investigation of fuel cell thermodynamics is necessary to understand their response to different environmental condition, a much more important question in pratical applications is: How does a fuel cell behave when it is loaded, i.e. when it actually has to do electrical work?

In this chapter we will disucss this questions by looking at the current-voltage-characteristics at different temperatures and pressures. As there exist no satisfying theoretical models for fuel cell kinetics, we will only use experimental data, which is of more practical interest anyway.

3.1 Temperature dependance of fuel cell kinetics

Figure 4 shows the I-U curves for temperatures of 40°C and 60°C. They were obtained at a pressure of 3 bar using pure oxygene as the cathode gas. Therefore the performance of the cell is better for higher temperatures. This was explained in detail in section 2.2 where we observed the same behaviour for the quiescent voltage.

The slope of the curves is steep for low currents. Here, the voltage drop is mainly caused by the transition overvoltage which results from the finite reaction speed.

For higher currents, the dominant factor is the ohmic resistance of the cell, indicated by an approximately linear slope of the I-U curve. The Ohmic overvoltage does not only depend on the resistance of the electrodes
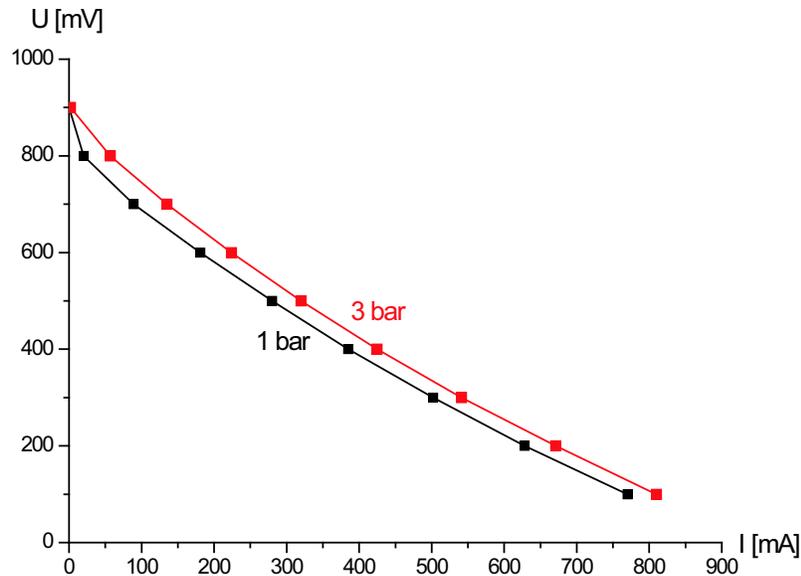
Figure 5: Current-Voltage curves of a loaded fuel cell for different gas pressures. The temperature was 60°C, the cathode gas was pure oxygene

but also on the energy loss that occurs during the transport of the H$^+$ ions through the membrane.

Another interesting observation is that the difference between the two curves increases for higher currents. This shows that some of the overvoltages are dependant on temperature. Probably the proton conductivity of the mebrane increases with temperature, thereby reducing the Ohmic overvoltage for higher temperatures.

3.2 Pressure dependance of fuel cell kinetics

In the previous section we have seen that a loaded fuel cell shows the same response to changes in temperature than an unloaded one. We might expect that this is also true for different pressures. Indeed, figure 5 shows that for higher pressures voltages are higher, too. The distance between the curves remains constant because the Ohmic overvoltage which is relevant here, does not depend on pressure.

The general shape of the characteristic curves is the same as in the previous section: A steep slope for low currents and almost linear behaviour for higher currents.

Much more interesting is the data shown in figure 6. This diagram compares fuel cell kinetics for air and pure oxygene as the cathode gas. As one would expect the performance of the cell is better for pure O$_2$, and for low currents the curves have the same shape as in the previous figures.

However, for high currents, a new effect appears when driving the cell with air: For high currents the voltage drop increases dramatically because the limited gas flow in combination with the low concentration of O$_2$ in air causes a lack of educts when too much power is requested. This effect is called the concentration overvoltage.

3.3 Power and Efficiency of fuel cells

From the current/voltage data discussed in the previous section, we can easily obtain the power of the fuel cell according to the equation $P = U \cdot I$. Figure 7 shows the results for air resp. pure oxygene as cathode gas. The diagram shows that there is an optimum current at which the cell is most powerful. For pure oxygene it is around 400 mA.

If one is interested in a very high power density, one would run the cell at this point. However, in most practial application, efficiency is more important than pure power. The efficiency ϵ is composed of several factors of which we will only consider the most important ones: The thermodynamical efficiency ϵ_{th}, which describes
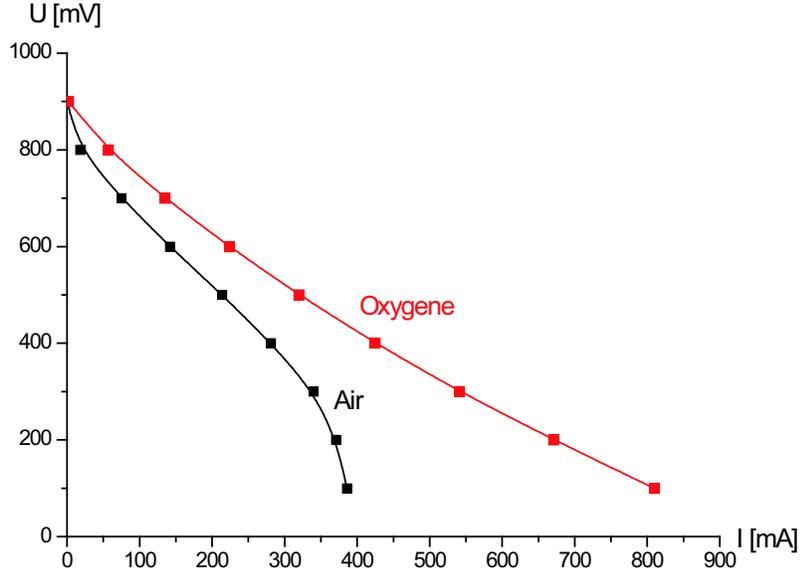
Figure 6: Current-Voltage curves of a loaded fuel cell for air and oxygene as cathode gases. The curves were recorded at a pressure of 3 bar and a temperature of 60°C.
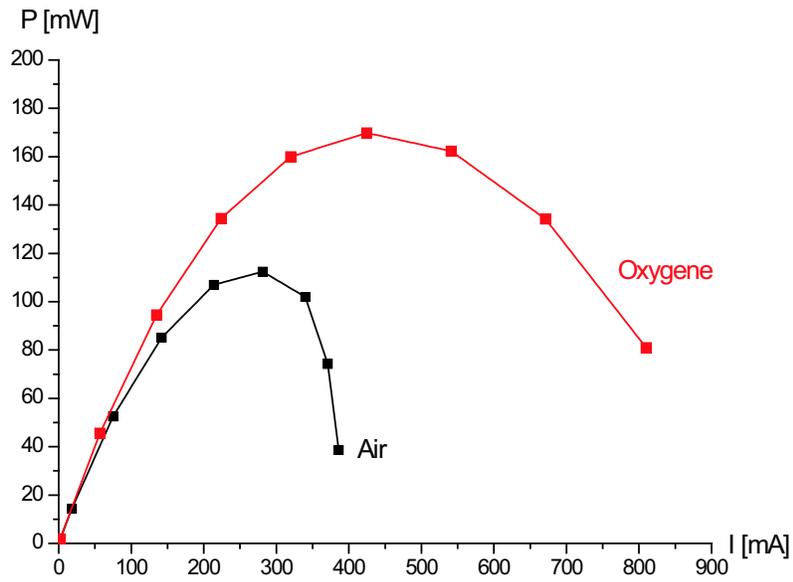

Figure 7: Power of a fuel cell for different currents. The curves were derived from the data shown in figure 6.
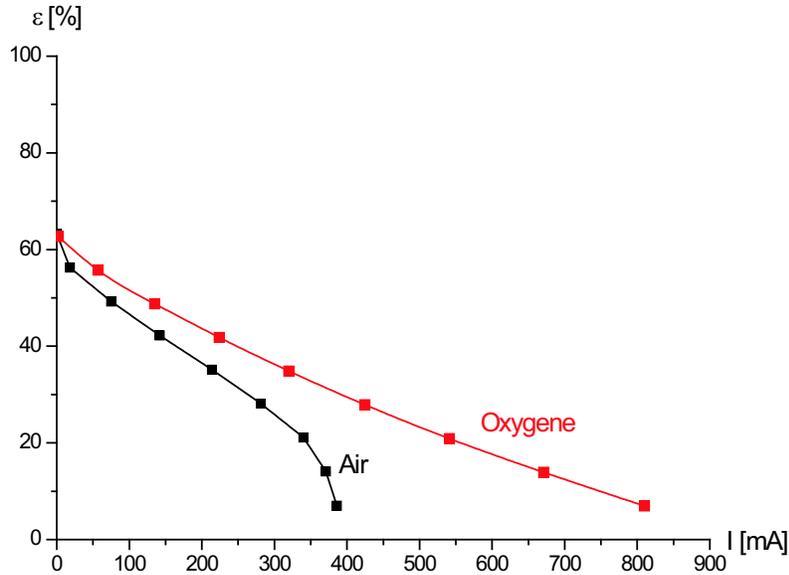
Figure 8: Efficiency of a fuel cell for different currents. The curves were derived from the data in figure 6.

the maximum efficiency that is allowed by the second law of thermodynamics, and the voltage efficiency ϵ_V, which indicates the loss that occurs due to overvoltages. They are defined by the following equations:

$$\epsilon_{th} = \frac{\Delta G}{\Delta H^0} = \frac{U^0 z F}{\Delta H^0} \tag{3}$$

$$\epsilon_V = \frac{U}{U^0} \tag{4}$$

Here, H^0 is the reaction enthalpy (272 kJ/mol), U^0 is the theoretical quiescent voltage and U is the actual quiescent voltage.

The total efficiency of the cell is the product of these two factors:

$$\epsilon = \epsilon_{th} \cdot \epsilon_V \tag{5}$$

One could take into consideration several other factors such as the percentage of fuel that leaves the cell without reacting, but for simplicity we will not do so.

Figure 8 shows the efficiency of our fuel cell over the current flow. The diagram shows that fuel cell efficiency can go up to 60% even for the relatively simple device we used. In comparison, a classical otto engine only reaches about 20%. For low currents, fuel cell efficiency is at a maximum. Therefore one might expect that it is best to run a fuel cell at the lowest current possible. However, as we saw in figure 7 the cell power is very poor in this region. Therefore, for practical applications, one must find a compromise between efficiency and power density.

4 Conclusions

Our experiments showed that fuel cells are an interesting alternative to fossil energy carriers, especially because of their high efficiency and the lack of toxic reaction products.

However, there are several drawbacks that spoil this positive result:

- The production of hydrogene in elctrolysers requires a lot of electrical energy, which, at the moment, cannot be produced using a "clean" technique.

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- Fuel cells are very expensive, mainly because of the platinum catalyst.

- A fuel cell is heavy. This greatly reduces its overall efficiency as an energy source for cars.

- As our experiments showed, there is no satisfying theoretical model for the complicated physical properties of fuel cells, so engineers have to rely on the principle of trial and error when designing fuel cells.

We can conclude that much more research has to be done before fuel cells will become a real alternative to fossile resources, but nevertheless they are one of the most promising solutions to many of the environmental problems of our time.