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INTERMITTENT OPERATION AND OPERATION MODELING OF AN ALKALINE ELECTROLYZER

W. HUG, H. BUSSMANN and A. BRINNER

German Aerospace Research Establishment, DLR, Institute for Technical Thermodynamics, Pfaffenwaldring 38-40, W-7000 Stuttgart 80, Germany

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Abstract—An advanced alkaline electrolyzer, developed for solar operation by the Research Centre Jülich, has been tested in various constant and intermittent operation modes for about 6000 h.

Based on this wide field of operating experience, the simulation model SIMELINT (SIMulation of ELectrolyzers in INTermittent operation) has been developed, calculating thermal behavior, cell voltage, gas purities and efficiencies for any given power or current profile. The results of the calculations with the model SIMELINT are in very good correspondence with measured constant and intermittent operation data, gained at the HYSOLAR 10 kW test and research facility in Stuttgart.

The code SIMELINT is a helpful tool for design and optimization of electrolyzers and for control strategies of intermittent electrolyzer operation.

1. INTRODUCTION

Within the joint Saudi Arabian-German research, development and demonstration program HYSOLAR for solar hydrogen production, a 10 kW test and research facility, including a complete system of energy conversion, hydrogen production, storage and operation control has been designed, realized and operated for about 3 years [1]. The main goals are the comparison of different power matching modes between photovoltaic generator and electrolyzer in intermittent operation and the optimization of subsystems [2]. Several alkaline electrolyzers have been constructed, operated and optimized. A 10 kW electrolyzer with 25 cells, developed by the Research Centre Jülich, shows very good performance and suitability for solar operation. Design criteria for the solar operated electrolyzer were high gas purity and current efficiency at partial load, low energy consumption and good dynamic response at intermittent load [3].

2. THEORETICAL AND EXPERIMENTAL BASIS FOR ELECTROLYZER MODELING

The simulation code SIMELINT was developed for optimization of electrolyzers and concepts for operation control strategies. This requires knowledge of the thermal behavior, power consumption, cell or block voltage, gas purities and current efficiency. The magnitudes of these characteristics are influenced by system temperature and, conversely, system temperature depends on these terms. The basis for electrolyzer modeling was the energy balance given below:

$$\dot{W}_{el} + \sum \dot{W}_{aux} + \sum \dot{Q}_v + \sum \dot{H} = 0. \tag{1}$$

For calculation of the first term, the electrical power consumption, we need information about the performance of electrodes, current efficiency and gas purities at the prevailing current density and temperature. They are discussed together with the other terms of the thermal balance equation in the following subsections. The simulation code has been evaluated up to now with the currently available experimental data of the 10 kW electrolyzer.

Performance of electrodes

To characterize the performance of the electrodes and to determine the specific power consumption, I-V curves have been recorded in the whole temperature range between 30° and 100°C. The performance of an electrolyzer can be divided into three parts: the reversible potential, the voltage drop due to the ohmic resistance of the cell and the anodic and cathodic overvoltages of the electrodes. The behavior of the electrolyzer after exchange of electrodes or diaphragms can be simulated by adaption of the corresponding share of the characteristic. The voltage record was fitted by the analytic function:

$$U = E_{rev} + A_1 i + A_2 \log i. \tag{2}$$

Through reducing the total characteristic by the linear amount, the iR-free share is obtained. A verification of this method for calculating iR-free voltages was made by measuring cell voltages in the currentless mode, and by electrode potential measurements [3]. The temperature dependence of the parameters A_1 and A_2 was gained by fitting with a polynomial of second degree. Figure 1 shows a surface plot of the recorded data as well as the area, which represents the calculated voltages in the investigated current density–temperature range.

Current efficiency

Current or Faraday efficiency is an important tool to determine the specific energy consumption of an electrolyzer, particularly at partial load. A current efficiency lower than 100% is caused by parasitic current losses along the gas and electrolyte ducts in the cell block. The decrease of the Faraday efficiency with decreasing current density is caused by the simultaneous increase of the parasitic current share along the gas ducts due to the increasing amount of electrolyte and, therefore, lower resistance. Parasitic currents are driven by the cell voltage, while the operating current is driven only by the difference between the cell voltage and reversible potential. Higher temperatures and, thus, lower resistance along the gas and electrolyte ducts cause worse efficiency.

Calculation of Faraday efficiency can be done with the shunt current method, but requires expenditure of computing time to determine each parasitic current in every cell of the electrolyzer block. Therefore, data for Faraday efficiency were obtained by measuring the hydrogen production rate at fixed current density and at constant temperature. A good correspondence between measured data and analytical description was obtained by fitting with the function given below:

$$\eta_F = B_1 + B_2 \exp\left(\frac{B_3 + B_4 T + B_5 T^2}{i}\right). \tag{3}$$

Figure 2 shows the measured current efficiencies as well as the surface plot which represents the calculated efficiencies in the range of validity, given in Section 3.

Purity of product gases

Gas purity at partial load is a necessary qualification criteria of intermittently operated electrolyzers. At low current densities, the purity of the product gases is significantly reduced by diffusion processes through diaphragms and sealings. Due to current efficiencies lower than 100%, gas production also takes place in the electrolyte and gas channels, increasing the share of impurities. Gas-tight diaphragms can reduce the amount of gas passing through the diaphragms remarkably. This benefit of higher gas purity is normally lowered by a higher specific energy consumption due to the elevated ohmic resistance.

Determination of gas purity on the basis of diffusion coefficient calculation is expensive and uncertain due to the unknown distribution of gas permeability over the cell block. Therefore, fitting of the measured amount of hydrogen in oxygen was used as a basis for modeling. Best agreement was obtained by using the function:

$$\begin{aligned} C_{H_2 \ln O_2} = {} & C_1 + C_2 T + C_3 T^2 \\ & + (C_4 + C_5 T + C_6 T^2) \\ & \times \exp\left(\frac{C_7 + C_8 T + C_9 T^2}{i}\right), \end{aligned} \tag{4}$$

for fitting in the range of validity given in Section 3. Measured gas impurities and the surface plot representing the calculated amount of hydrogen in oxygen in the investigated current density–temperature range are shown in Fig. 3. This figure illustrates a strong increase of the gas impurities with decreasing current density and a slight increase with increasing temperatures. The higher amount of hydrogen in oxygen at higher temperatures is

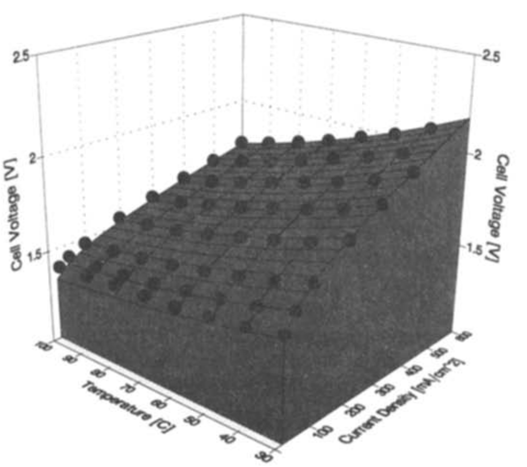

Fig. 1. Measured and calculated electrode performance.

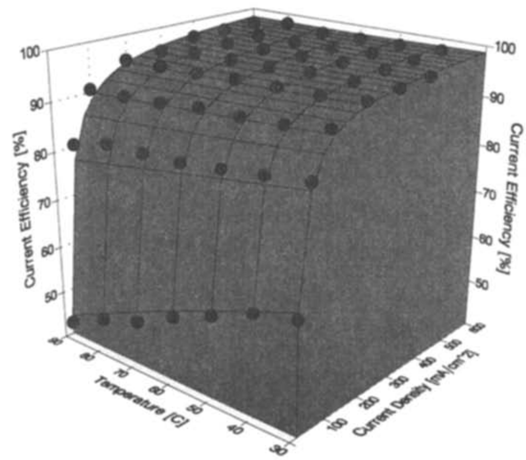

Fig. 2. Measured and calculated current efficiency.

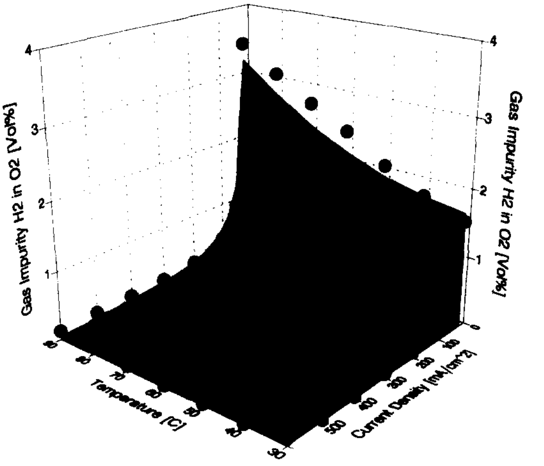

Fig. 3. Measured and calculated amount of hydrogen in oxygen.

caused by the higher diffusion velocity at elevated temperatures.

A slight dependence of current density and no significant dependence of temperature concerning the content of oxygen in hydrogen could be observed in Fig. 4. This amount never exceeds 0.2% and can therefore be neglected in operation modeling.

The gas purities have been determined following a current-density-dependent delay time of up to 120 min due to the volume of the gas separators. This delay time between gas production and gas analysis was considered in the model, assuming a complete mixture of the gases entering the separators with purities according to the present current density and temperature in the cell block and those inside the separators.

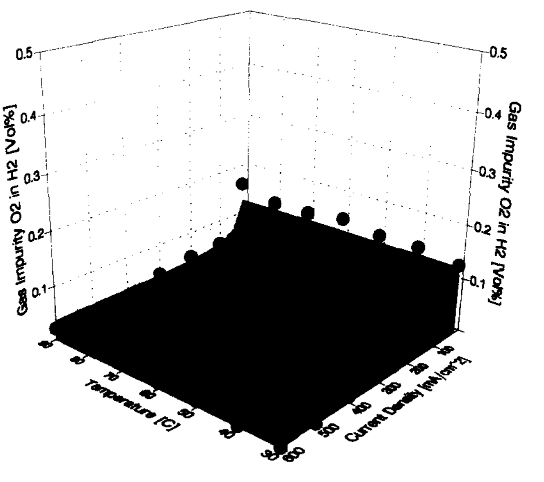

Fig. 4. Measured and calculated amount of oxygen in hydrogen.

Auxiliary power consumpion

Additional auxiliary power consumption lowers the total efficiency of the electrolyzer. Maintaining of the potential is necessary to avoid corrosion of the activated electrodes at shut-off times. The temperature-dependent current for potential stabilization is in the range of between 1 and 4 A. In order to avoid shutdown of the system during solar operation round the clock due to bad gas purity, this current level was elevated to 10 A. To promote electrolyte circulation, a pump has been installed in the electrolyzer periphery. No significant temperature dependence of power consumption for pumping was observed. In the model, a power consumption for electrolyte circulation of 200 W was considered.

Power consumption for control and supervision of the electrolyzer was neglected in the calculations.

Enthalpies and heat losses

Enthalpies of feed and cooling water, water vapor, hydrogen and oxygen are calculated at the prevailing temperature and pressure of the system and the surroundings, respectively, referred to standard conditions of 25°C and 1013 mbar.

Determination of heat losses by conduction, convection and radiation was done with calculation formulas given in Ref. [4]. A detailed discussion of the thermal and mass balance of the electrolyzer used was discussed in a seminar project report [5].

3. THE PROGRAM SIMELINT AND ITS LIMITATION

The variable inputs for simulation of electrolyzer operation are 24 h data files with current or power profiles on the basis of 2.5 min values. In the latter case, current is calculated iteratively using the characteristic for electrode performance and a starting value for system temperature. In the following, temperature is changed, calculating electrode characteristic, current efficiency, gas purity, enthalpies and heat losses after every temperature step until equation (1) is fulfilled. The program lists and stores these values and starts by reading the next current or power value up to the end of the data file. Then the program returns with the calculation of accumulated energy consumption, hydrogen production and the total efficiency. Time periods with potential maintenance are treated separately in the calculation and the listing. Simulations of single and multiple day operation are possible. The final calculated daily values are used as starting values for the following day.

The model does not consider different temperature distributions in the system components. All calculations are referred to the temperature inside the cell block. This temperature was also the basis for all experimental measurements. Ambient and system conditions are considered as constant within the operation periods.

Experimental investigation and therefore system modeling validity are limited to a current density range of 50–600 mA cm^{-2} corresponding to 20–120% of nominal load and to a temperature range of 30°–90°C at ambient pressure.

4. VERIFICATION OF THE MODEL AND SIMULATION RUNS

Constant operation

First verification of the simulation code SIMELINT was reached in the constant operation mode. Comparison of data gained in real constant operation of the electrolyzer with simulation results showed very good correspondence. For example, at constant operation with 400 mA cm^{-2} starting at a system temperature of 50°C, the electrolyzer reached a final temperature of 73°C and a corresponding block voltage of 44 V after 13 h of operation. Calculations of temperature and voltage courses with identical boundary conditions showed a maximum deviation of 1°C and 400 mV, respectively, from real operation data.

Solar operation

The reference for verification of simulating intermittent operation was a sequence of 2 days with solar operation of the PV-electrolyzer system in 1991. Operation started on 28 August at 00:00 and ended on 29 August 23:59 without interruption. Time periods with elevated current for potential maintenance were 00:00–06:30 and 18:30–23:59 each day.

The results of real operation and calculation with SIMELINT are summarized in Figs 5 and 6 for 28 August. Figure 5 shows insolation and current profiles for this day with few dynamics, as well as the good correspondence between recorded and calculated block voltage. Recorded and calculated courses of temperature and the amount of hydrogen in oxygen are compared in Fig. 6, again showing good conformity. Total efficiency for this day was 0.63, related to the lower heating value of hydrogen.

Some of the corresponding results for the following day are given in Fig. 7, a day with significant dynamics.

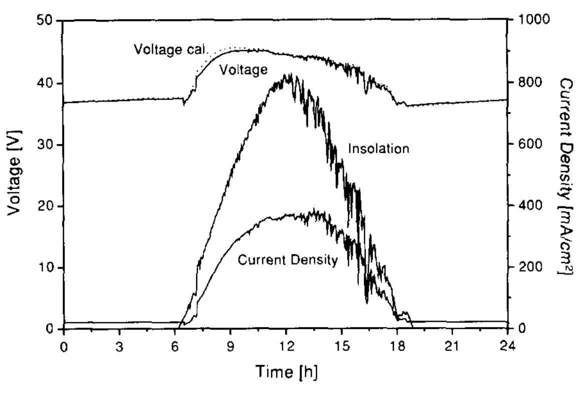

Fig. 5. Comparison of recorded and calculated block voltage.

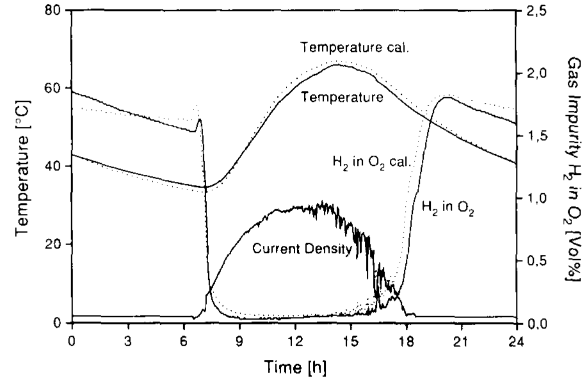

Fig. 6. Comparison of recorded and calculated temperature and gas purity.

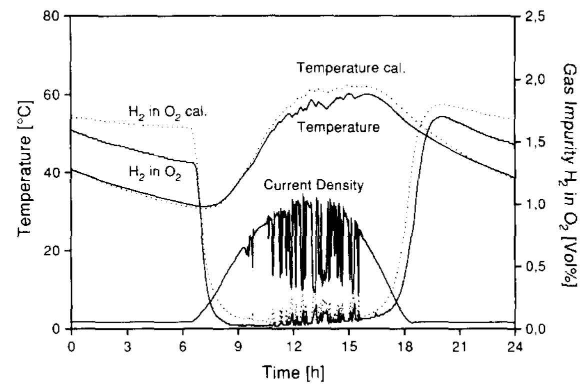

Fig. 7. Comparison of recorded and calculated temperature and gas purity.

Final values of the previous day were used as starting values in the calculation. The calculated maximum temperature is slightly higher compared with the recorded system temperature. A possible reason is the fact that ambient temperature was considered as constant in the calculation, whereas changes in ambient temperature of ± 3°C could be observed. A total efficiency of 0.62 was calculated.

Simulated operation with photovoltaic current and wind energy converter power profiles

To eliminate the influence of the modeling input with discrete current profiles on the basis of 2.5 min values, the electrolyzer has been operated in the simulated operation mode. A controllable grid-connected rectifier with external PC-controllable current set point was used to supply the electrolyzer with an identical discrete current profile to that applied to the simulation code.

Discrete current profiles, derived from real operational data of the above-presented days were used as input for modeling as well as for simulating solar operation. Calculation runs with variation of system starting temperature between 20° and 60°C show good agreement with data recorded during electrolyzer operation. The results are given in Fig. 8.

In the following, calculations using different current scaling factors between 0.5 and 1.4 of the recorded current profiles are performed by SIMELINT. Again, a good correspondence between calculated and recorded system data were obtained. Results of a calculation run and the corresponding electrolyzer operation data, using the current profile of 29 August increased by 25%, are presented in Fig. 9. For this day a total efficiency of 0.63 was calculated.

Recent calculations were run with output power profiles of the 100 kW wind energy converter DEBRA [6], scaled down to 10% to agree with the nominal load of the electrolyzer. The current supply was fed with the standardized power profile, providing corresponding voltage and current for the electrolyzer according to the prevailing system temperature. Figure 10 gives the results of the calculation and the recorded operational data for the ouput power profile of the wind energy converter on 15 January 1990. A rather good agreement between the current profile supplied to the electrolyzer and the calculated current profile was obtained. Compared with the recorded system temperature, the calculated temperature course was slightly higher.

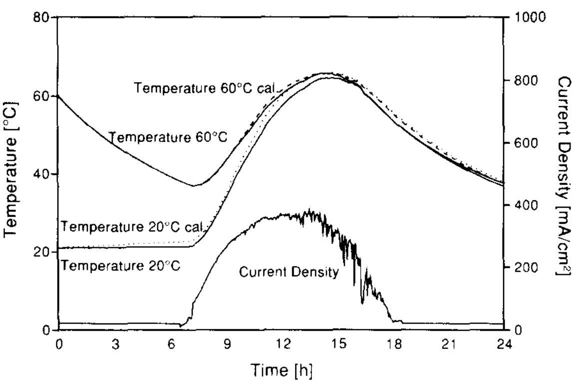

Fig. 8. Simulation runs with variation in starting temperature.

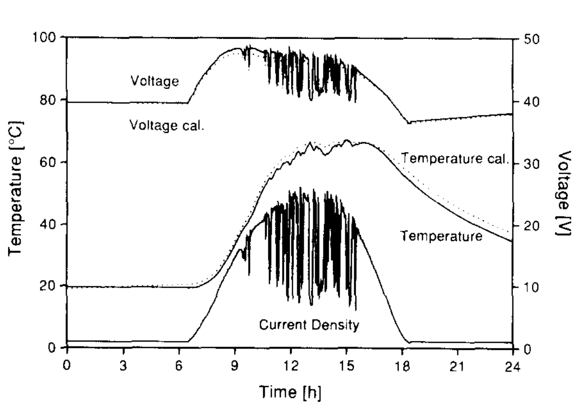

Fig. 9. Simulation run with a current scaling factor of 1.25.

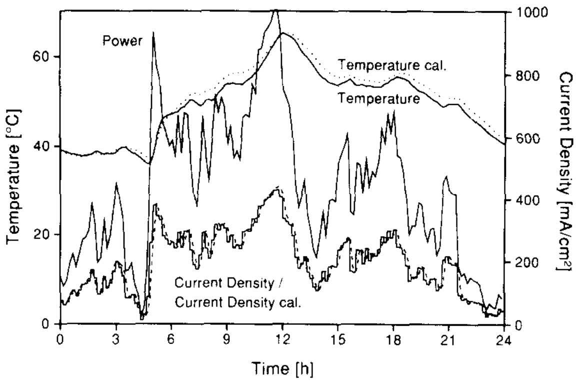

Fig. 10. Simulation run with a scaled down power profile of a wind energy converter.

5. CONCLUSIONS

Simulation gives important assistance to experimental work as it allows us to analyze and generalize the results of measurements, and to consider different boundary conditions and parameter variations. The simulation code SIMELINT was verified in different constant and intermittent operation modes, showing good suitability for electrolyzer modeling. The required basis was an analytical description of the system behavior, obtained by fitting of measured values. The accuracy of all calculations was related to the quality of fitting. Calculations of voltage, temperature, gas purity and system efficiency for any given current or power profile were in good correspondence with data recorded during system operation. Temperature differences within the system, change of ambient conditions during operation and influence of pressure were not considered in the simulation code. This will be part of future work.

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