Hydrogen and Storage
Research Center

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Enhancement of Alkaline Pressure Electrolysis System Performance

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9th International Freiberg Conference on IGCC & XtL Technologies
3 – 9 June 2018, Berlin, Germany

AGENDA

1 INTRODUCTION: PRESSURE ELECTROLYSIS AT THE HYDROGEN RESEARCH CENTER

2 PRESSURE AND TEMPERATURE DEPENDENCE ON CELL VOLTAGE

3 MEASUREMENT RESULTS

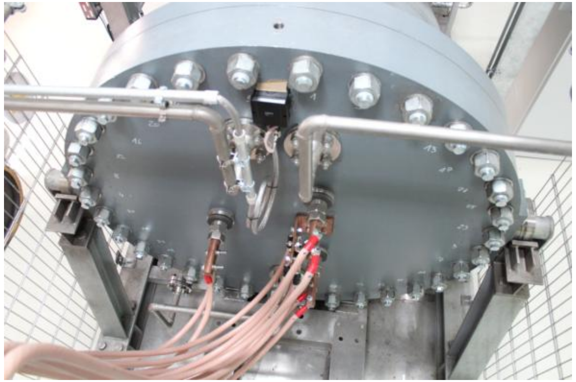
4 ENERGETIC COMPARISON

5 SUMMARY

INTRODUCTION: PRESSURE ELECTROLYSIS

Research electrolyser

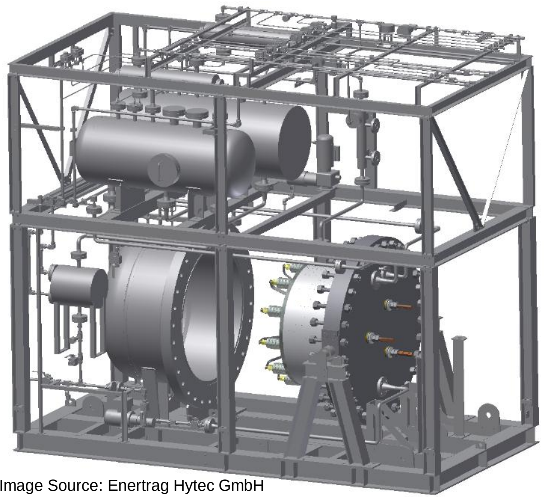
- 20 Nm^3/h nominal hydrogen production rate
- 24 single cells – filter press design
- Operating pressure max. 58 bar
- Operating temperature 75 °C
- Current density up to 7.2 kA/m^2
- Partial load 10 %
- Fast response time:
  - 50 A/s
  - ~ 60 s to max. power (warm stand-by)



INTRODUCTION: PRESSURE ELECTROLYSIS

Pressure vessel and stack

- External pressure vessel – filled with demineralised water
- Zirfon®-diaphragm
- Electrolyte: Potassium hydroxide solution 28 wt.-%
- High efficient electrodes
  - Cathode: Raney nickel
  - Anode: Nickel
  - Perforated electrodes (0.44 m^2 each)



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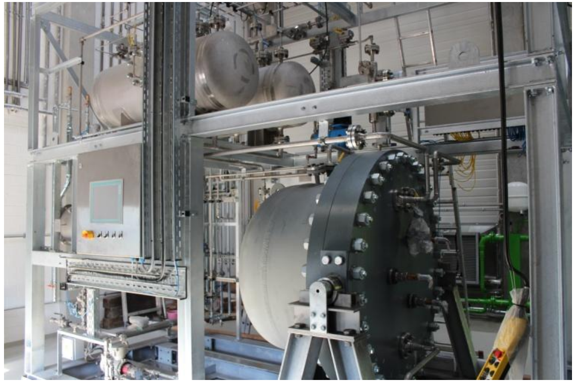

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PRESSURE AND TEMPERATURE DEPENDENCE

Reversible cell voltage – temperature dependence

$$dG = -S\,dT + V\,dp$$

$$\frac{\partial \Delta_R G_m^0}{\partial T} = -\Delta_R S_m^0$$

$$\frac{\partial U_{rev}}{\partial T} = -\frac{1}{2F}\frac{\partial \Delta_R G_m^0}{\partial T} = \frac{\Delta_R S_m^0}{2F} = \frac{163.3\,J\,K^{-1}\,mol^{-1}}{2 \cdot 96\,485\,A\,s\,mol^{-1}} = 0.846\,\frac{mV}{K}$$

	Electrolysis of water
Reversible Cell Voltage	ΔU_{rev}^0 = - 1.229 V
Entropy change	ΔS^0 = 0.1631 kJ K^{-1} mol^{-1}
Temperature coefficient	0.85 mV K^{-1}

- Further temperature induced decrease of cell voltage by
  - Enhanced conductivity of electrolyte and membrane
  - Enhanced catalytic activity and exchange current density
  - Lower activation overpotential at electrodes

PRESSURE AND TEMPERATURE DEPENDENCE

Reversible cell voltage – pressure dependence

$$dG = -S\,dT + V\,dp$$

$$\frac{\partial \Delta_R G_m^0}{\partial p} = \Delta V_m^0$$

$$\frac{\partial U_{rev}}{\partial p} = -\frac{1}{2F}\frac{\partial \Delta_R G_m^0}{\partial p} = -\frac{\Delta V_m^0}{2F}$$

- Inserting ideal gas law and integration:

$$U_{rev}(p) = U_{rev}(p_0) - \frac{RT}{2F}\ln\left[\left(\frac{p_{H_2}}{p_0}\right)\left(\frac{p_{O_2}}{p_0}\right)^{1/2}\right]$$

(valid for electrolysis of water, H_2 and O_2 pressurised)

	Electrolysis of water
Reversible Cell Voltage	ΔU_{rev}^0 = - 1.229 V
Pressure coefficient	- 44 mV/dec (at 25 °C)

PRESSURE AND TEMPERATURE DEPENDENCE

Reversible cell voltage – pressure dependence

- Assumption: only cathode side pressurised

$$\Delta U_{rev} = \frac{RT}{2F} \ln\left(\frac{p_{H_2}}{p_0}\right)$$

- Additional compression work

$$\Delta W = Q \times \Delta U_{rev} = n \times 2F \times \frac{RT}{2F} \ln\left(\frac{P_{H_2}}{P_0}\right) = nRT \ln\left(\frac{P_{H_2}}{P_0}\right)$$

→ Same work with ideal isothermal compression

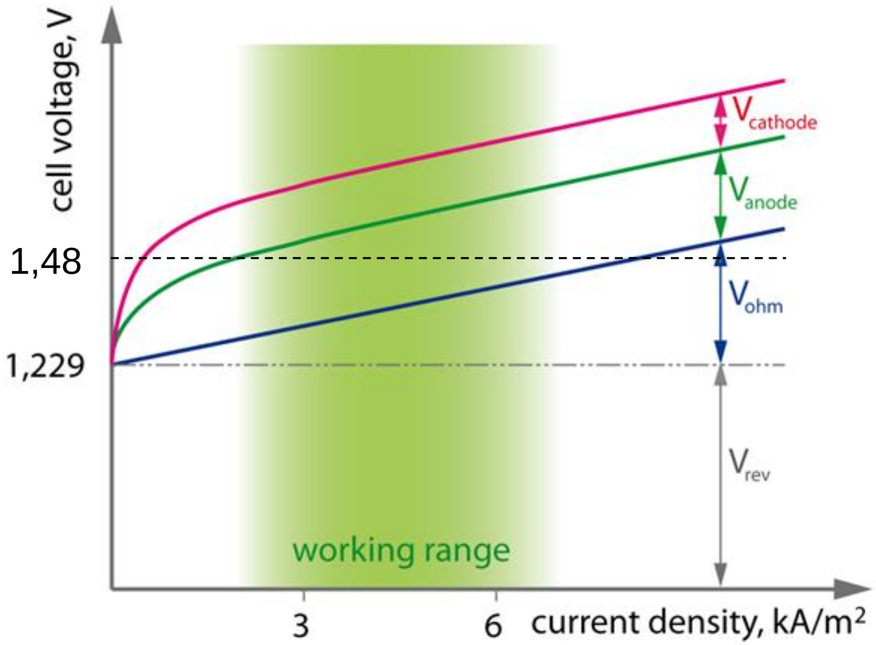
→ Real compressor more scope to inefficiencies

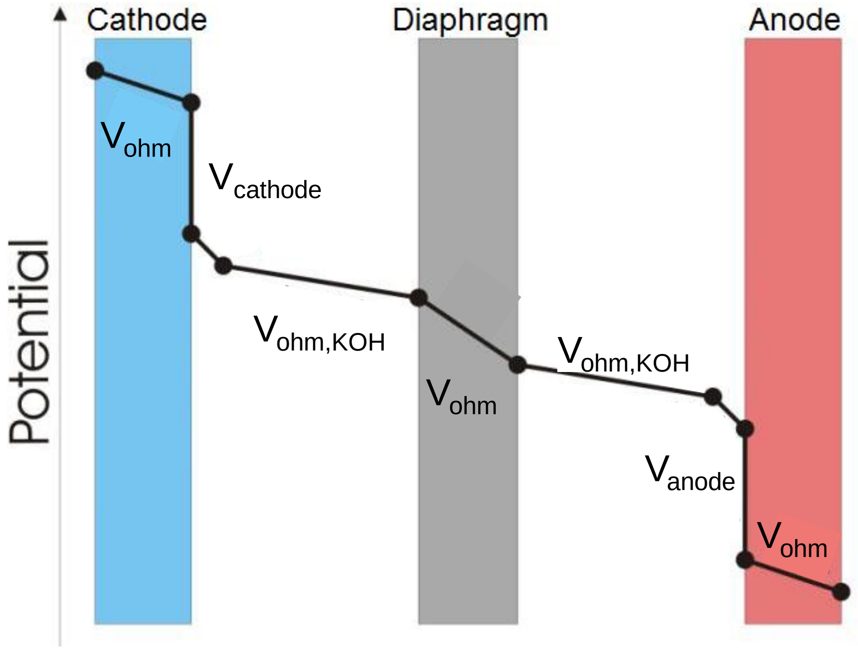
	Electrolysis of water
Pressure coefficient	- 30 mV/dec (at 25 °C)

PRESSURE AND TEMPERATURE DEPENDENCE

Overvoltages in real irreversible case

$$U_{cell} = U_{rev} + U_{an} + U_{cath} + U_{ohm}$$



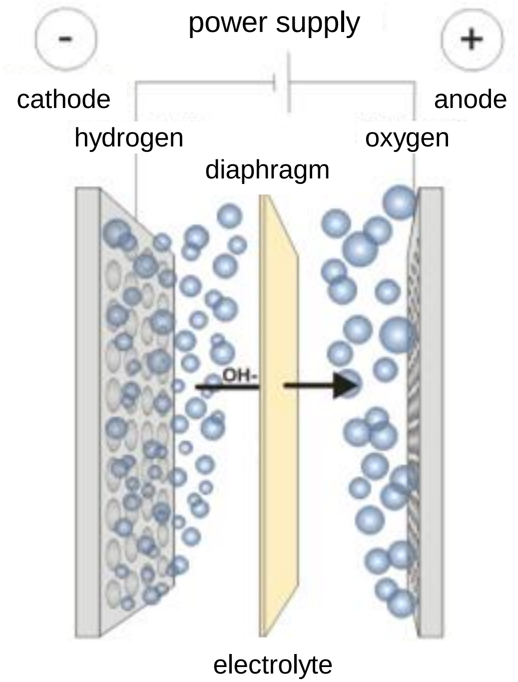


PRESSURE DEPENDENCE

Pressure electrolysis – bubble influence

Increasing pressure	
Positive influence	**Negative influence**
Decreasing bubble diameter → Decreasing ohmic resistance	Decreasing bubble diameter → Lower buoyancy force → Lower velocity of ascent → Bubbles stay longer in lye → More difficult to detach bubble from electrode surface

- To optimize
- Gap width (minimal resistance vs. optimal bubble flow)
- Gap geometry
- Surface morphology
- Flow velocity
- Avoid mass transport limitation (concentration overvoltage)
- Uniformity of current density



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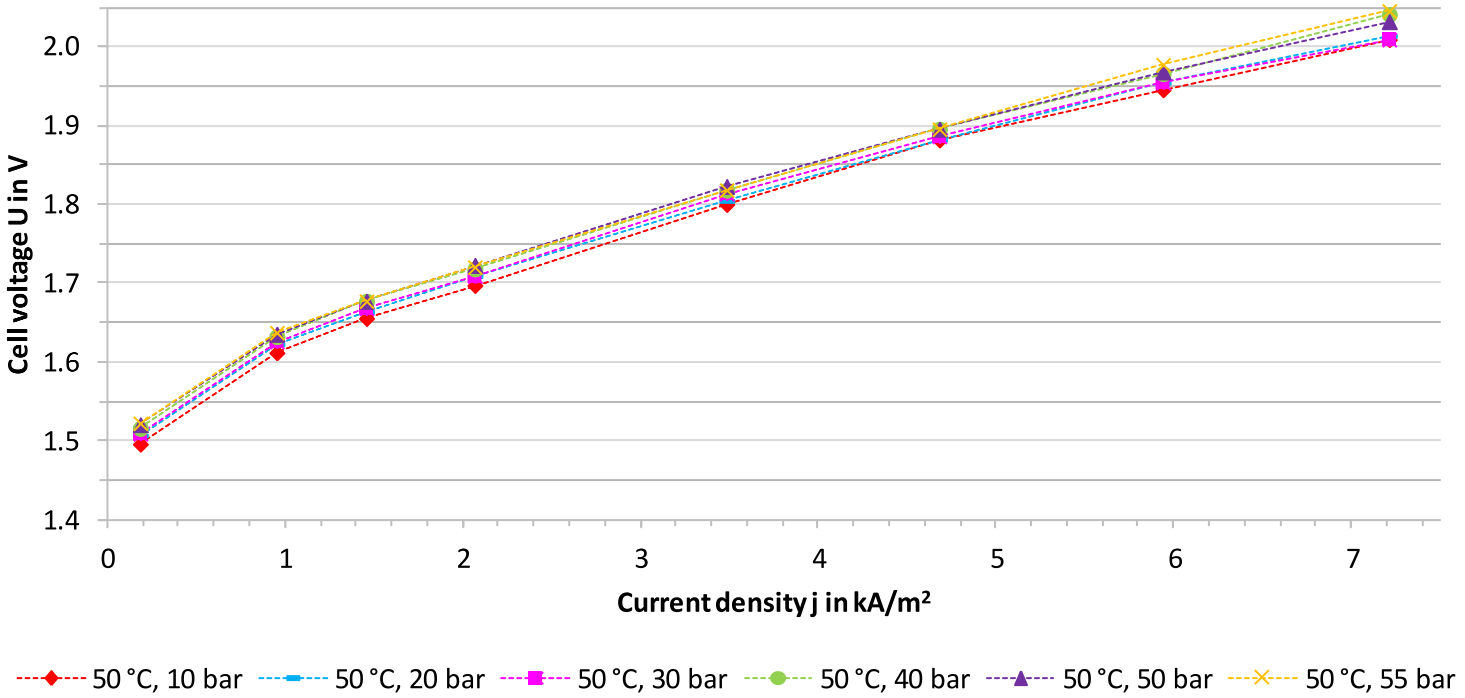
MEASUREMENT RESULTS

Measurement conditions

- Pressure: 10; 20; 30; 40; 50; 55 bar
- Temperature: 50; 60; 70 °C
- Current density: 0.18; 0.95; 1.46; 2.07; 3.48; 4.68; 5.94; 7.21 kA/m^2
- Electrolyte flow rate constant at 800 l/h
- Residence time interval for each measurement: max. 5 min.
- No external cooling for minimal temperature difference between stack inlet and outlet
- Reference temperature: stack outlet, hydrogen site
- Cell voltage: mean value of series connection of 22 cells

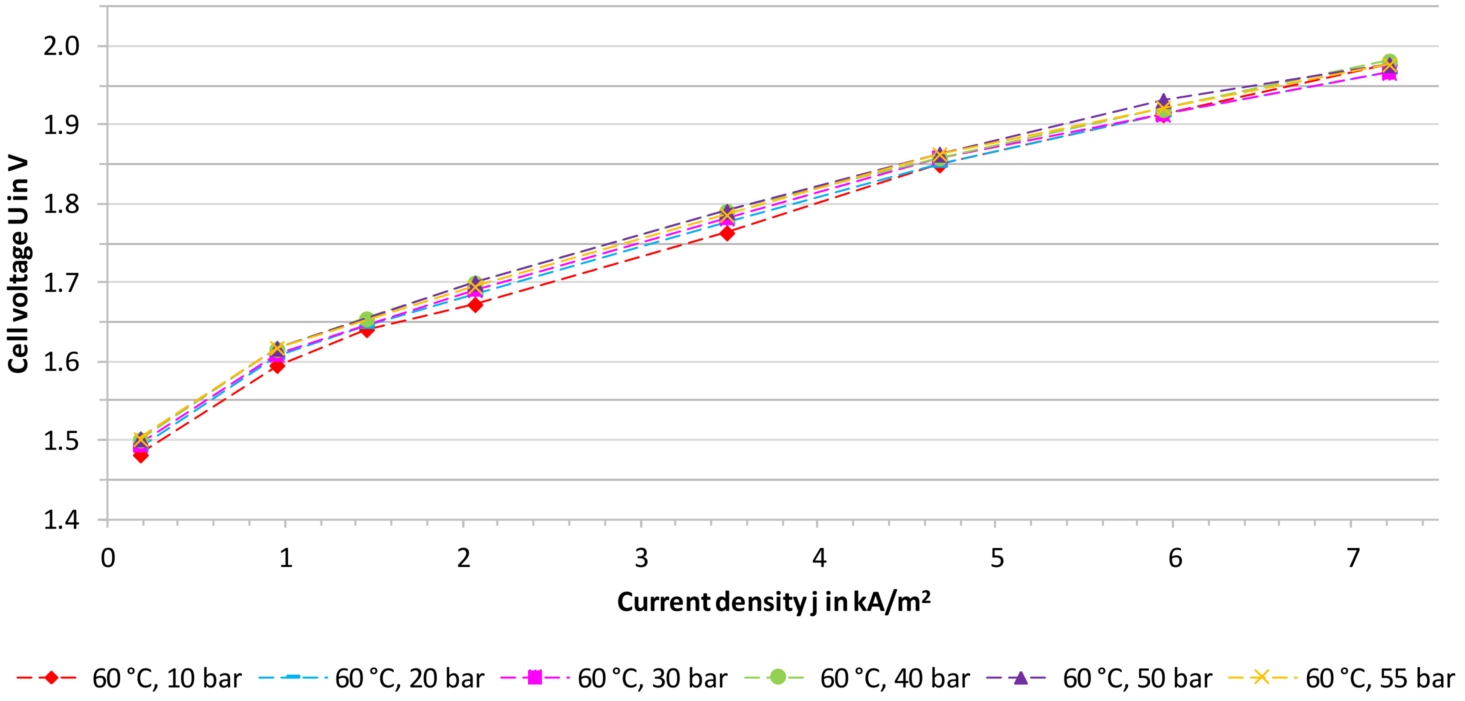
MEASUREMENT RESULTS

Pressure dependent j-U curve at 50 °C



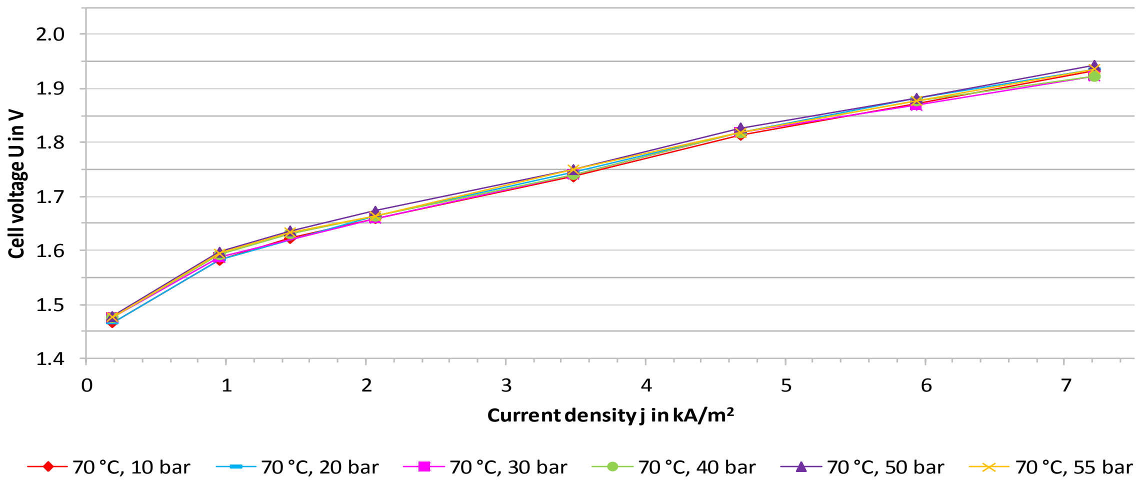
MEASUREMENT RESULTS

Pressure dependent j-U curve at 60 °C



MEASUREMENT RESULTS

Pressure dependent j-U curve at 70 °C



- Only marginal pressure influence on stack voltage for all temperatures and current densities

⇒ Slight increase of cell voltage

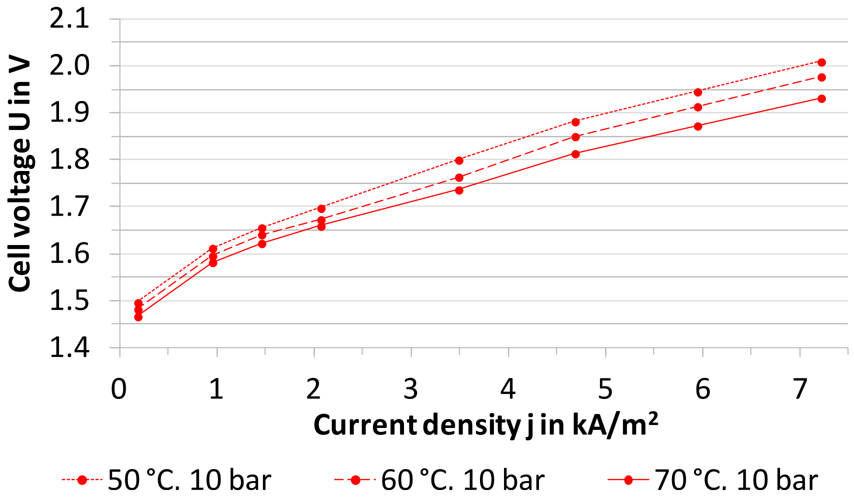
- (U_{55bar} – U_{10bar} ~ 0.02V)

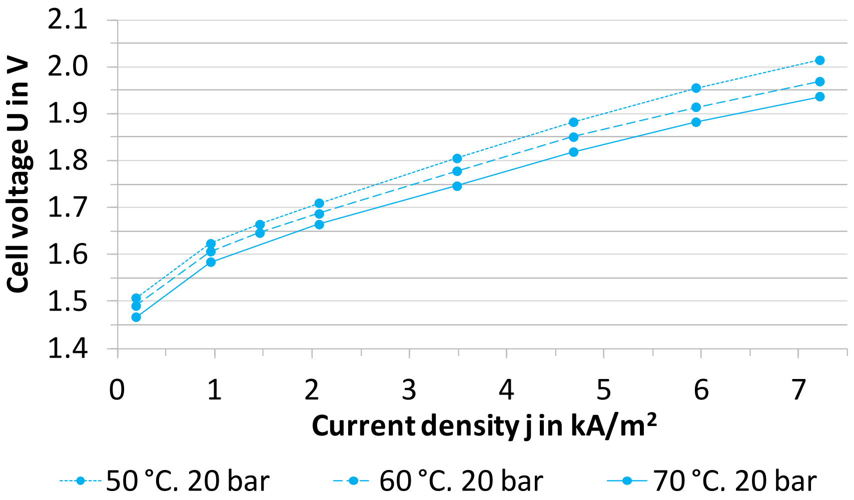
⇒ But decrease of cell overvoltage

- 0.023 V

MEASUREMENT RESULTS

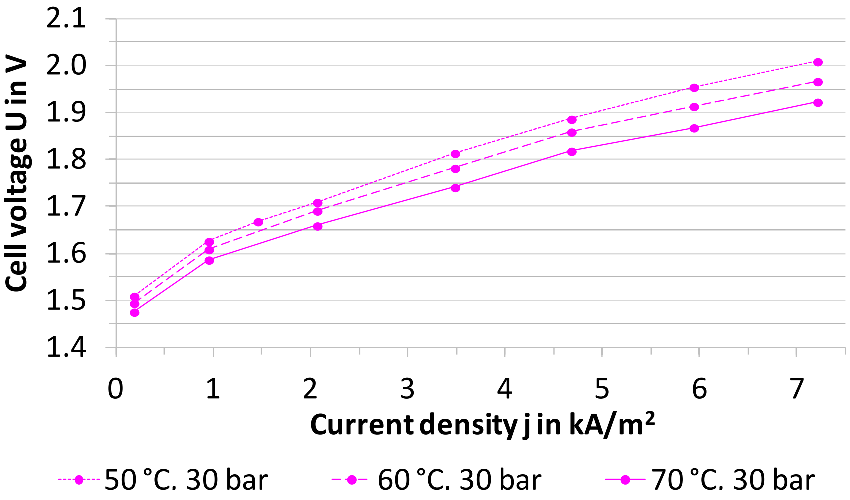
Temperature dependent j-U curves at 10 bar and 20 bar

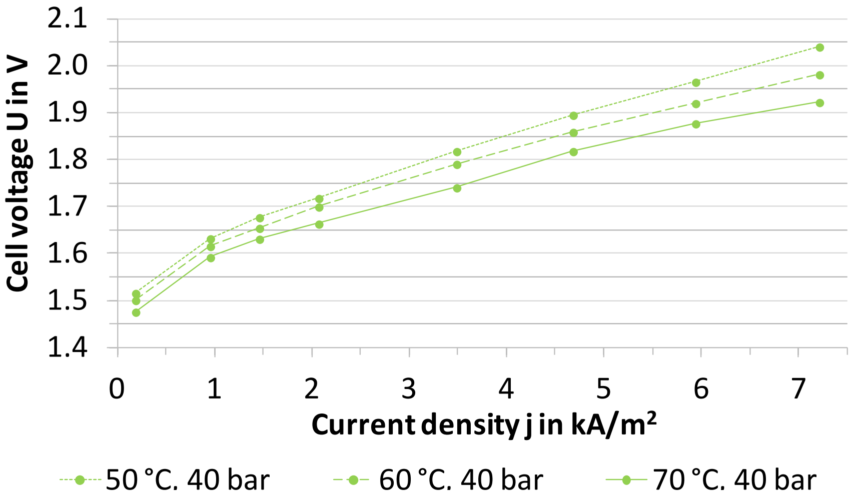




MEASUREMENT RESULTS

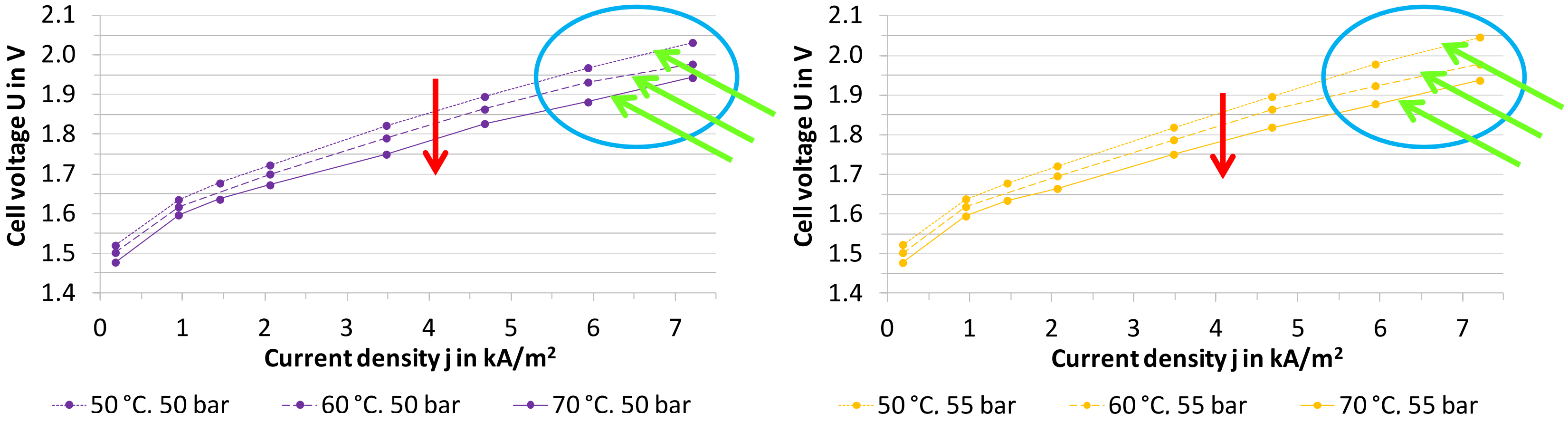
Temperature dependent j-U curves at 30 bar and 40 bar





MEASUREMENT RESULTS

Temperature dependent j-U curves at 50 bar and 55 bar



→ Significant temperature influence on cell voltage for all pressures and current densities

- → Distinct decrease of cell voltage and cell overvoltage with temperature
  - → 1.9 mV/K (at 0.2 kA/m²) up to 4.6 mV/K (at 7 kA/m²)
- → Electrolyte resistance accounts for only one third of the temperature dependency
- → Generally more pronounced at high current densities
- → Lower slope of the curves at higher temperatures

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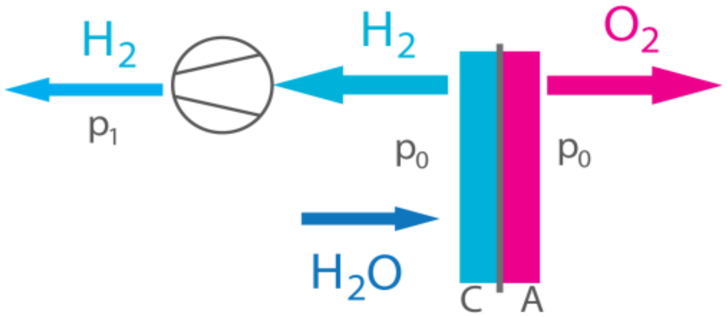
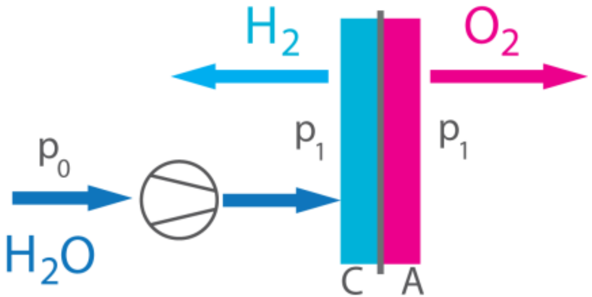
ENERGETIC COMPARISON

Atmospheric electrolysis vs. pressure electrolysis -1

Atmospheric electrolysis with subsequent compression



Pressure electrolysis with water boost pump



Practical approach for comparison:

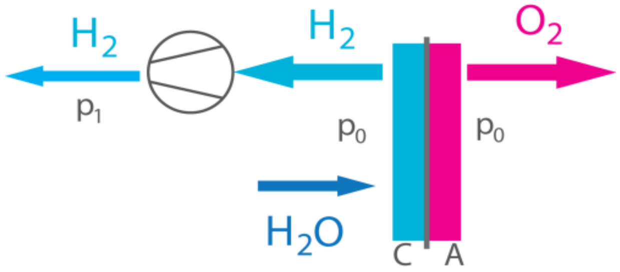
- Because of practical independence of stack voltage from pressure we compare only additional energy for:

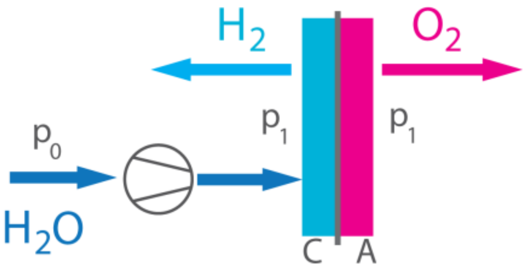
Hydrogen compression

water boost pump

ENERGETIC COMPARISON

Atmospheric electrolysis vs. pressure electrolysis - 2





Hydrogen compression

$$w_{compr} = \frac{w_{compr,rev}}{\eta_{mech} \cdot \eta_{isen}} = \frac{c_p \cdot m \cdot T_0}{\eta_{mech} \cdot \eta_{isen}} \left(\left(\frac{p_1}{p_0} \right)^{\frac{\kappa - 1}{\kappa}} - 1 \right)$$

water boost pump

$$w_{pump} = p_1 \cdot \Delta V_{H_2O}$$

With T_0 =298 K, η_{mech} = 0.98, η_{isen} = 0.75
final pressure p_1 = 60 bar:

w_{compr} = 0.33 kWh ⇐ per 1 m³ hydrogen (at STP) ⇒ w_{pump} = 0.014 kWh

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SUMMARY

- Distinct temperature influence on cell voltage
  - 1.9 mV/K (at 0.2 kA/m²) up to 4.6 mV/K (at 7 kA/m²)
  - Only one third of the influence caused by pure electrolyte conductivity
- Measurements: Only marginal pressure influence on cell voltage due to opposite effects
  - Result in coincidence with other authors
- Energetic comparison of pressure and atmospheric electrolysis
  - Atmospheric electrolysis: Hydrogen compressor w_{compr} = 0.33 kWh/m^3
  - Pressure electrolysis: Water boost pump only w_{pump} = 0.014 kWhm^3
  - From this point of view pressure electrolysis advantageous

Thank you for your kind attention!

Image Source: Mercedes-Benz B-Klasse F-Cell

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INTRODUCTION PRESSURE ELECTROLYSIS

- System components
  - Feed water system
  - Cooling system
  - Rectifier
  - Gas drying and purification system

- Pressure control systems
  - Pressure balance control between H_2 and O_2 separators
  - Pressure balance control between stack inside and surrounding