UNDERSTANDING PEP

Part 1: Mechanisms, Chemistry, Parameters

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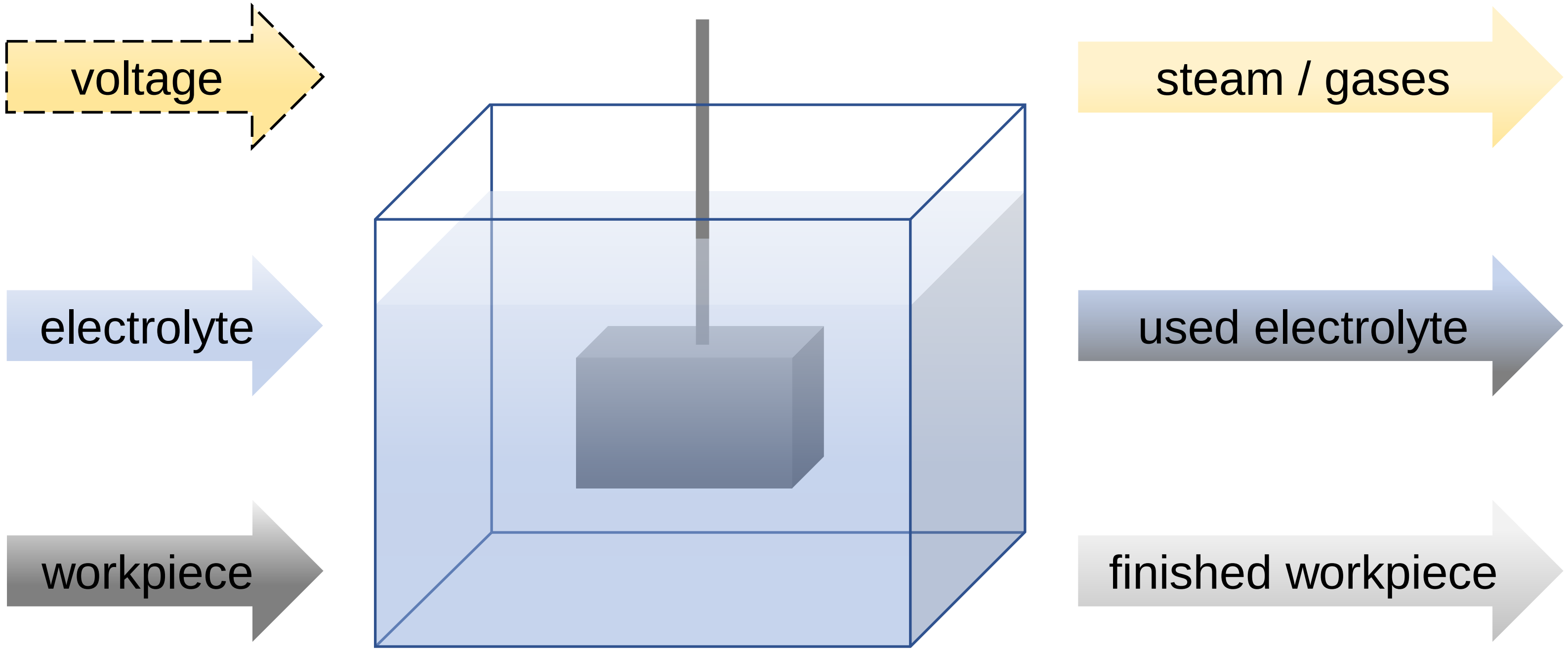
Understanding Pep


voltage

electrolyte

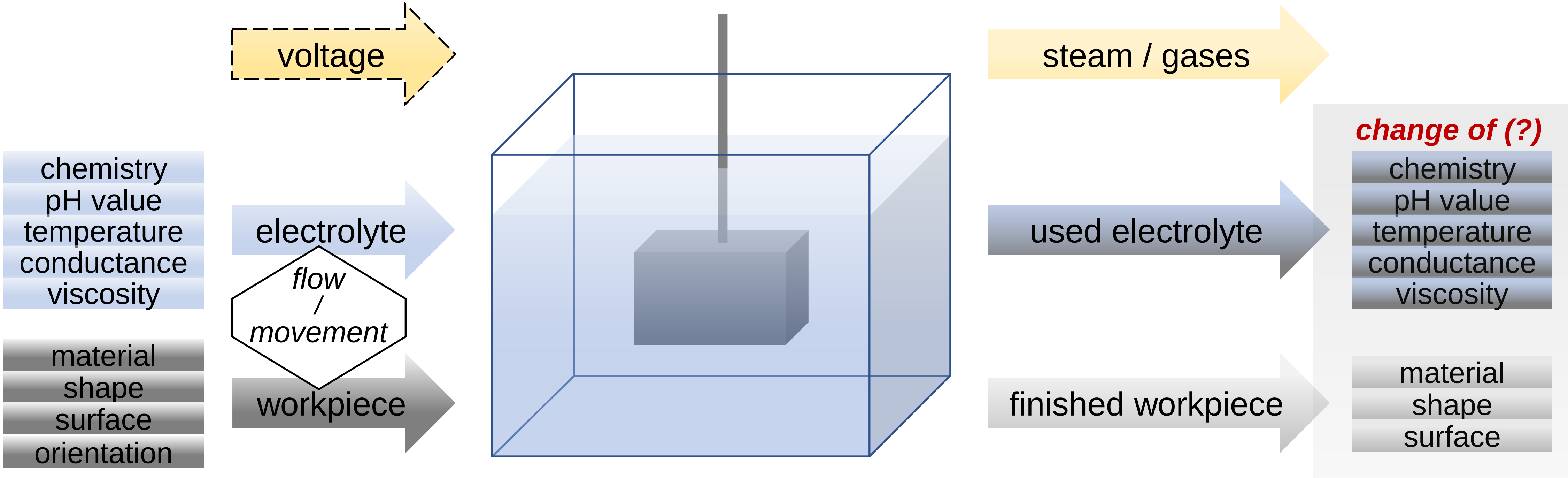
workpiece

steam / gases

used electrolyte

finished workpiece

Understanding Pep



chemistry
pH value
temperature
conductance
viscosity

material
shape
surface
orientation

voltage

electrolyte

flow / movement

workpiece

steam / gases

used electrolyte

finished workpiece

change of (?)

chemistry
pH value
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material
shape
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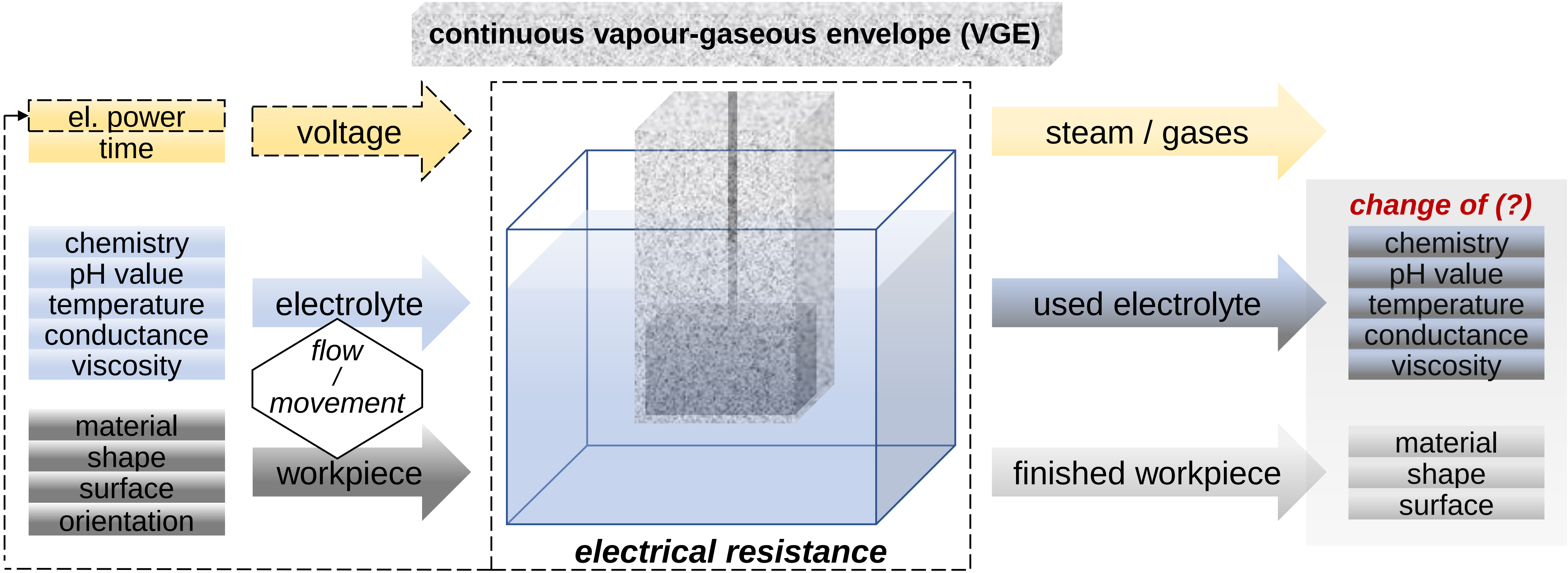
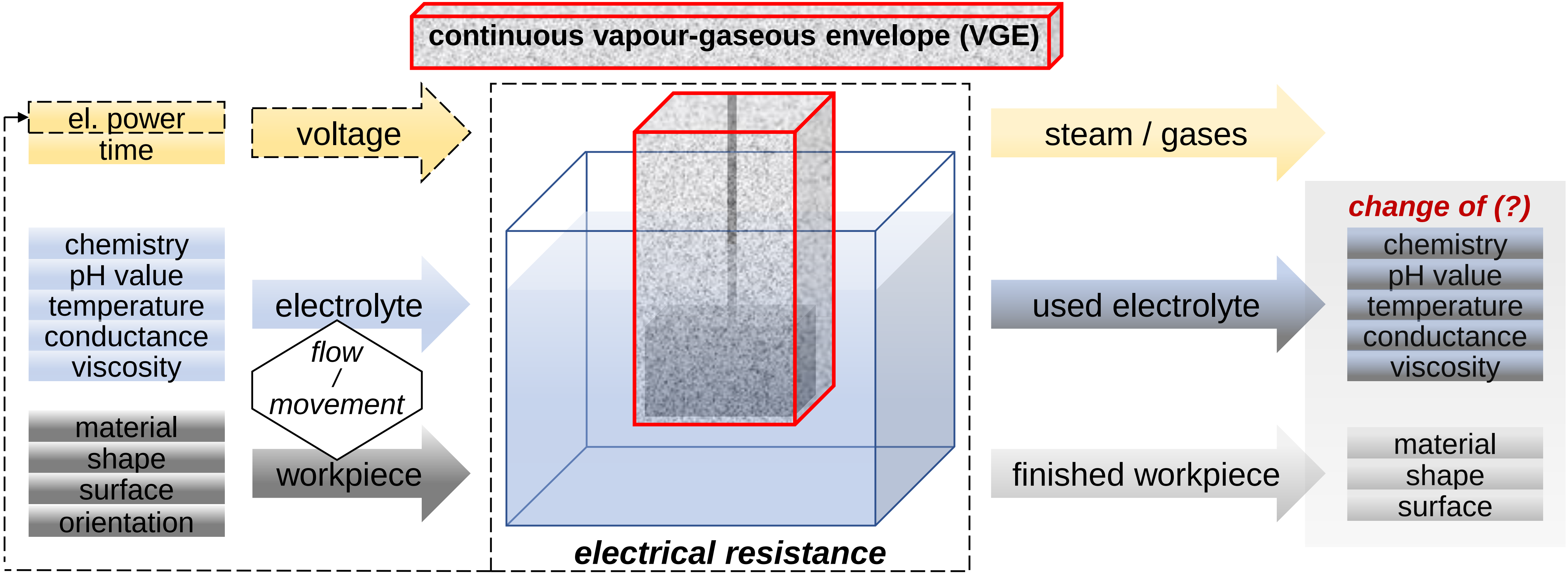
(not) a simple process with complex relations?!

Understanding Pep



Special feature: Plasma forms under atmospheric pressure in liquid

Understanding Pep vapour-gaseous envelope (VGE)



continuous vapour-gaseous envelope (VGE)

el. power
time

voltage

chemistry
pH value
temperature
conductance
viscosity

electrolyte

flow / movement

material
shape
surface
orientation

workpiece

electrical resistance

steam / gases

used electrolyte

finished workpiece

change of (?)

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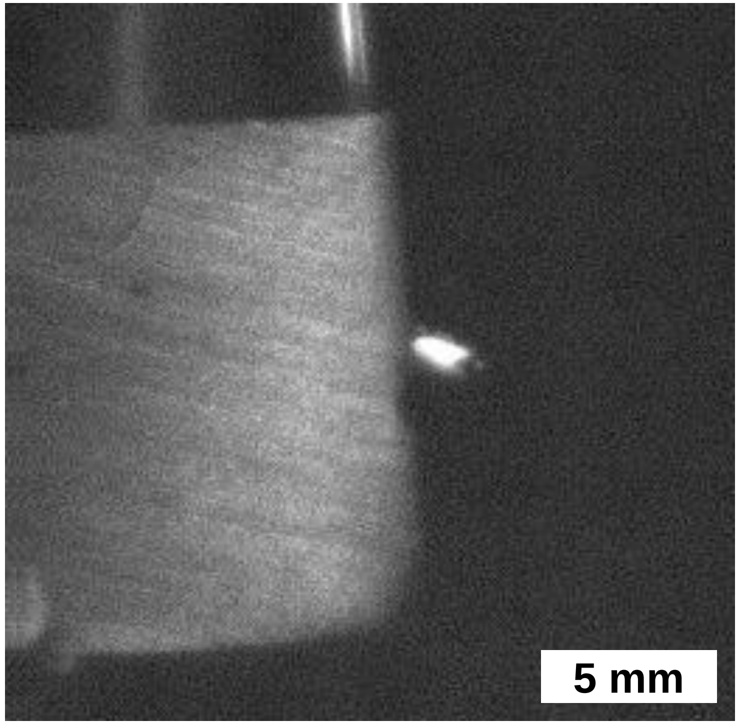
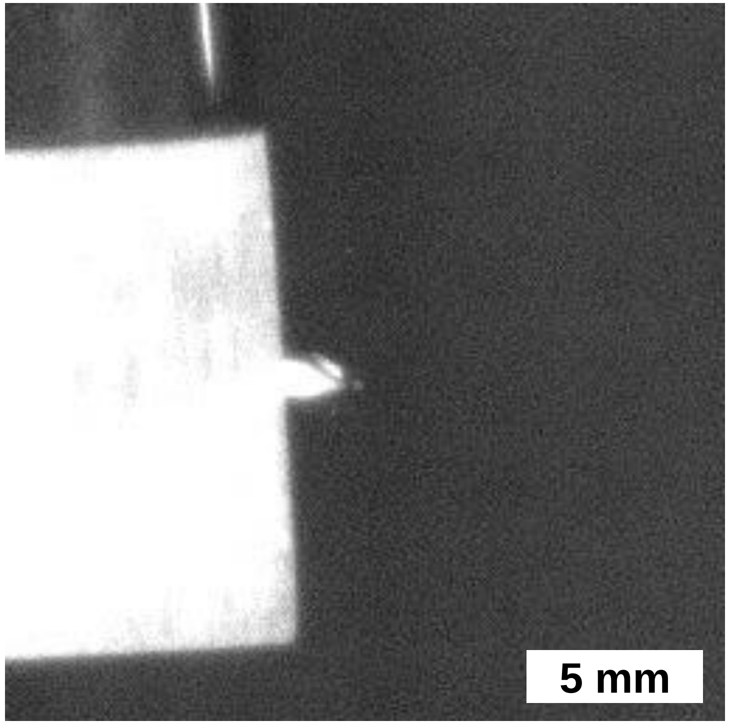
Understanding Pep

Developement of VGE

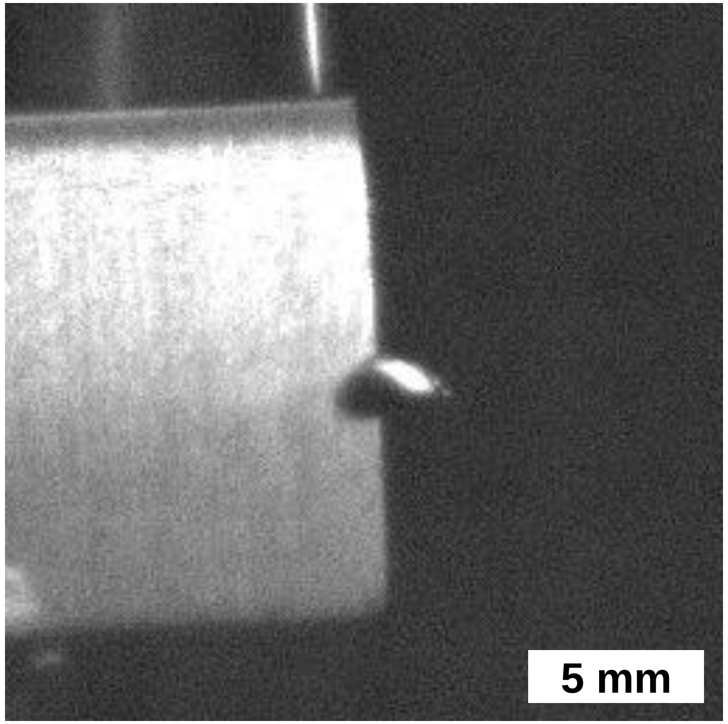
High-speed Camera recordings starting submerged: 0.0 ms ≤ t ≤ 8.33 ms



316 V



340 V



360 V

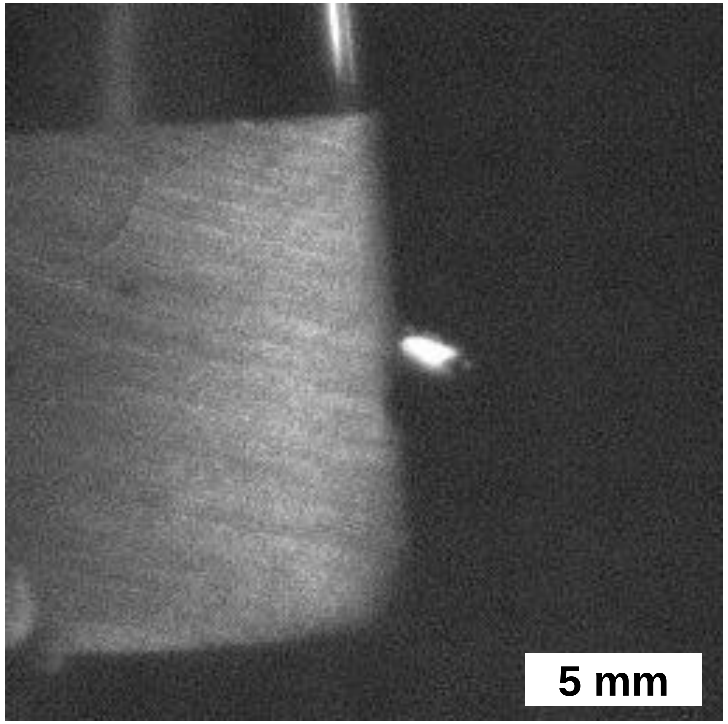
→ Very fast and high hydrodynamic process

Understanding Pep

Developement of VGE

High-speed Camera recordings starting submerged: 0.0 ms ≤ t ≤ 8.33 ms

→ t = 0 ms



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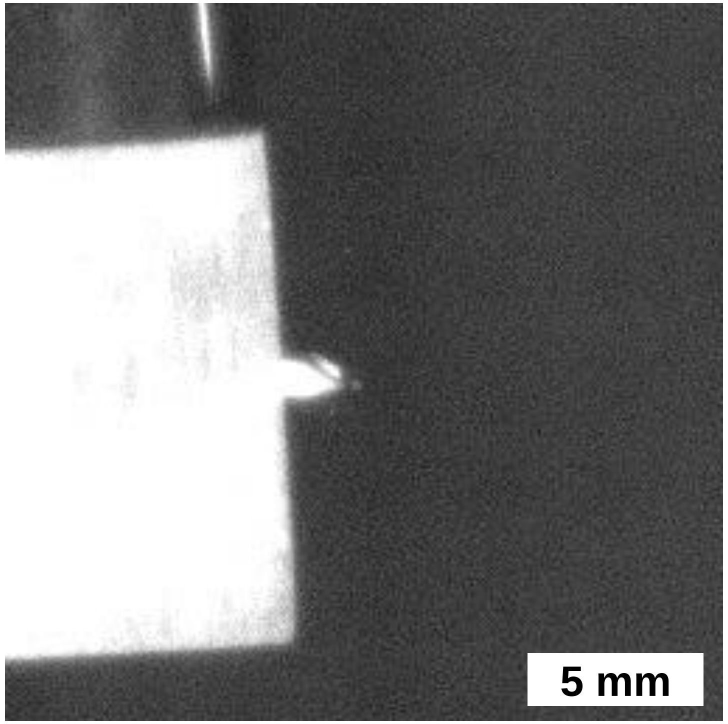

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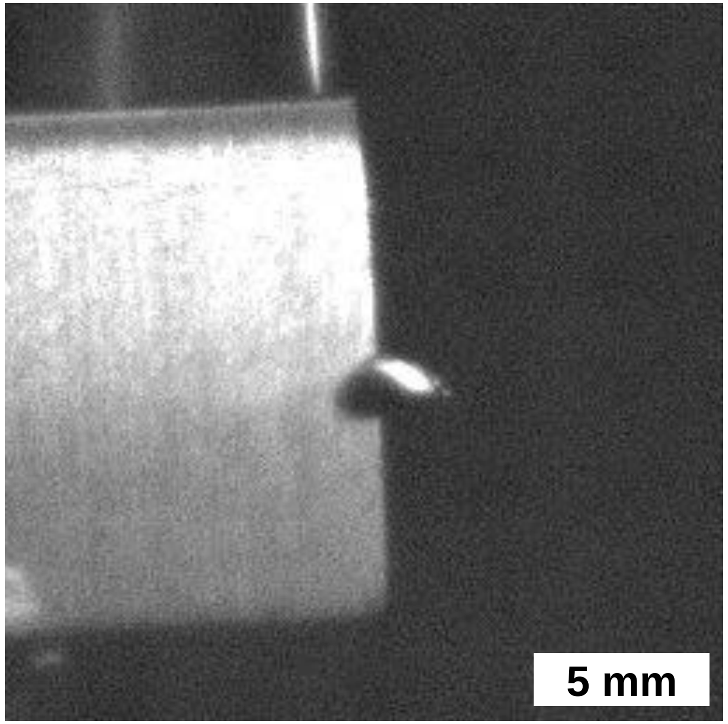

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Developement of VGE

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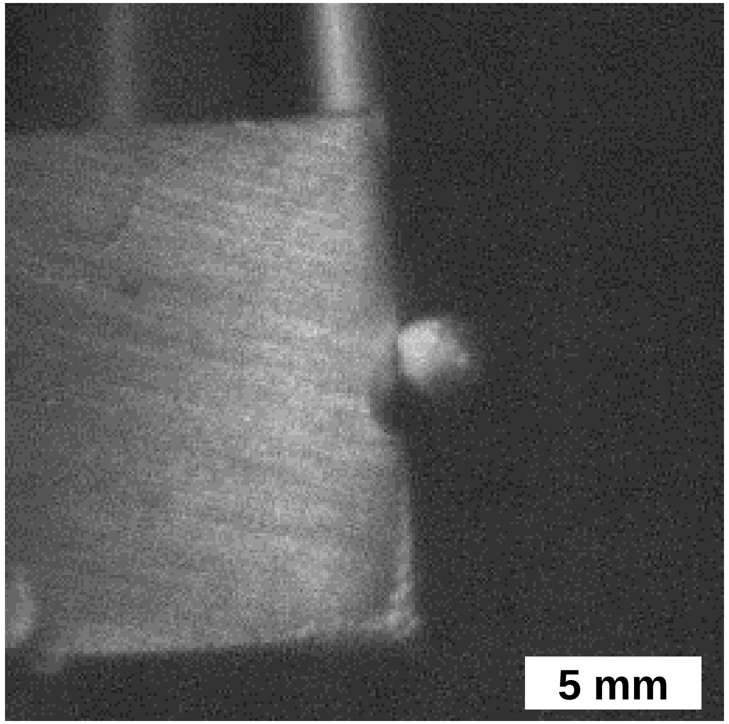
→ t = 0.33 ms



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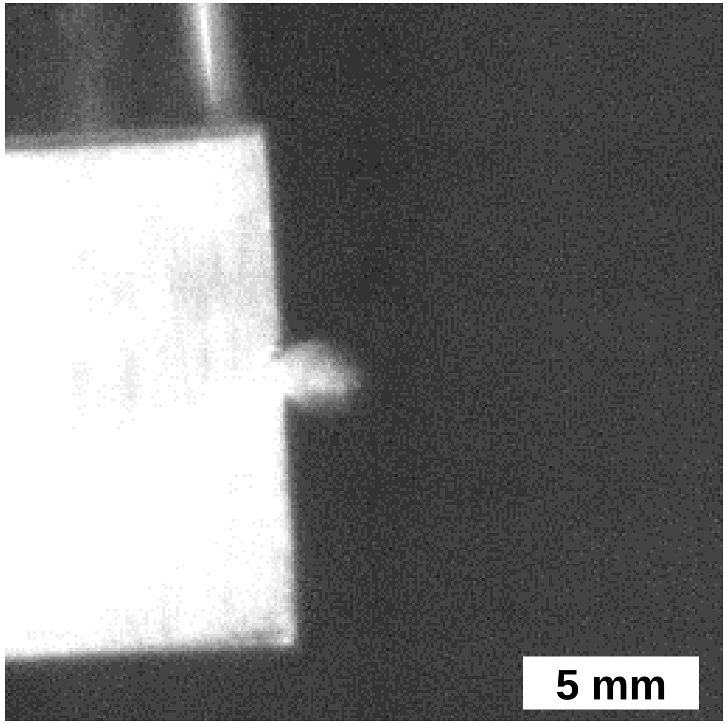

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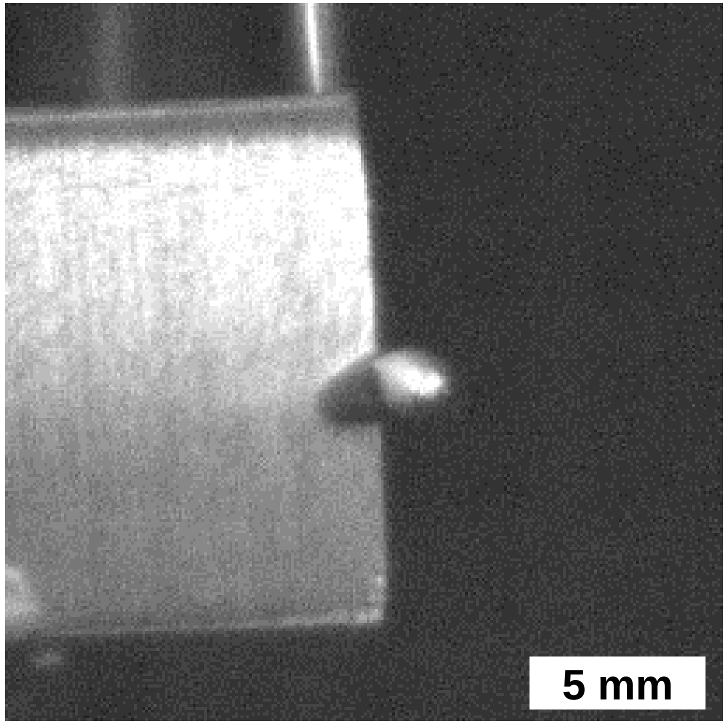

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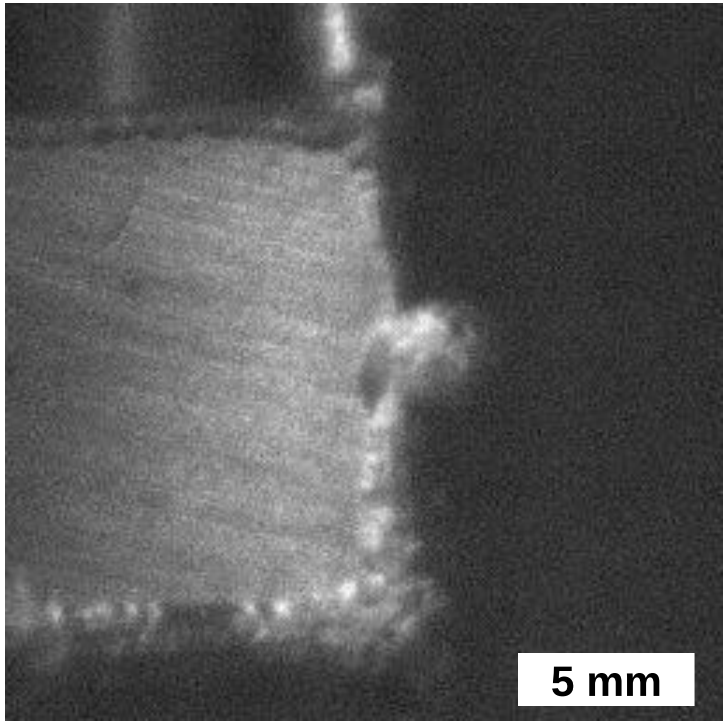
Understanding Pep

Developement of VGE

High-speed Camera recordings starting submerged: 0.0 ms ≤ t ≤ 8.33 ms

→ t = 1 ms



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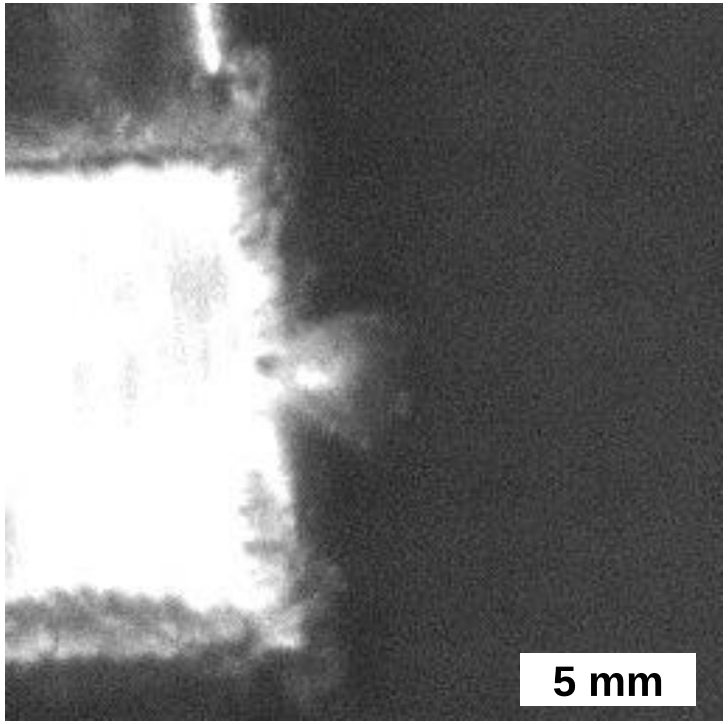

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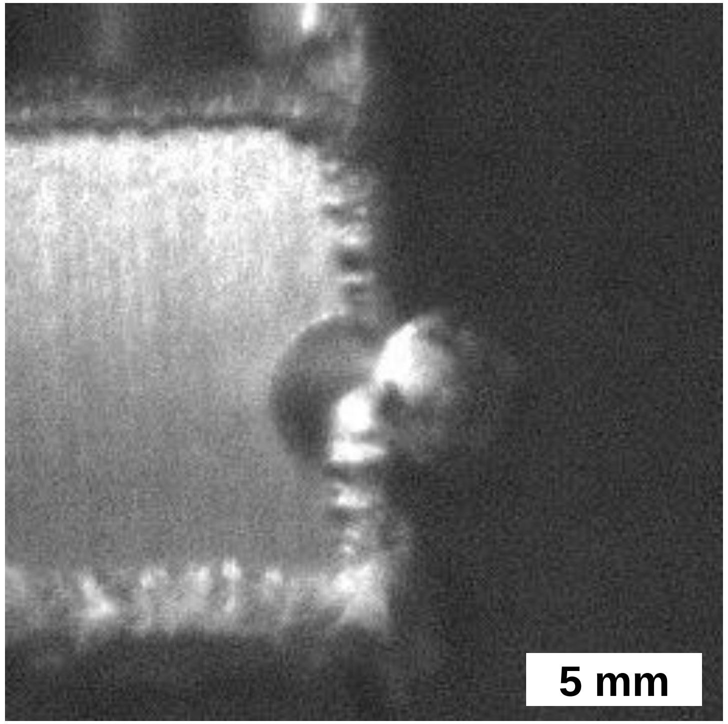

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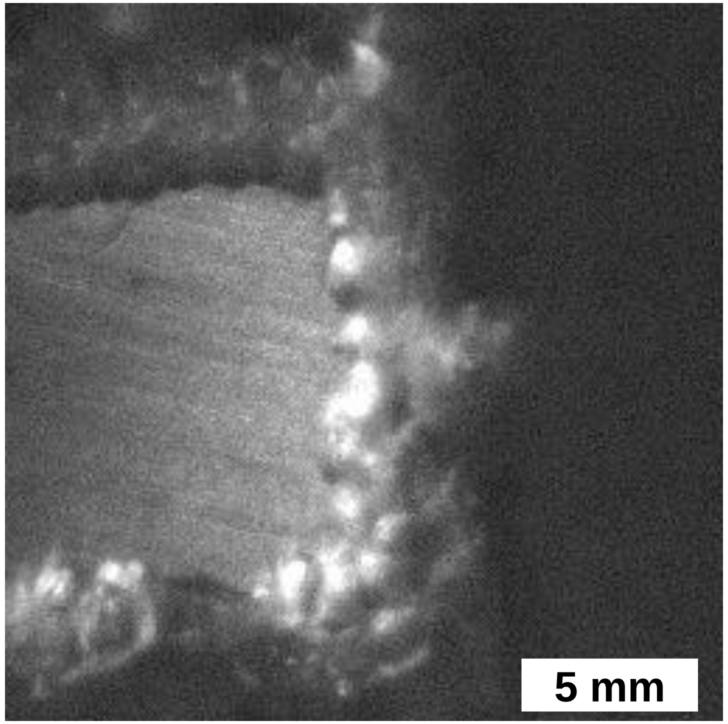
Understanding Pep

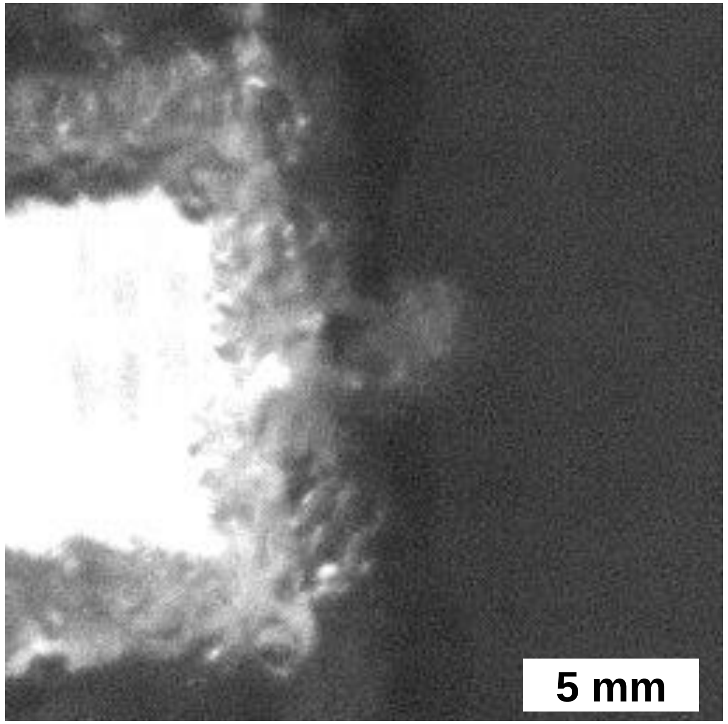
Developement of VGE

High-speed Camera recordings starting submerged: 0.0 ms ≤ t ≤ 8.33 ms

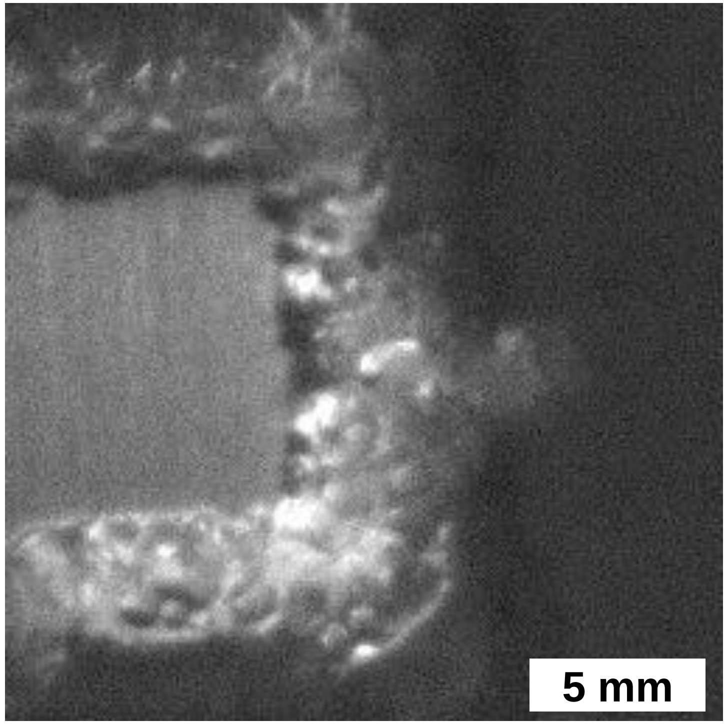
→ t = 2 ms



316 V



340 V



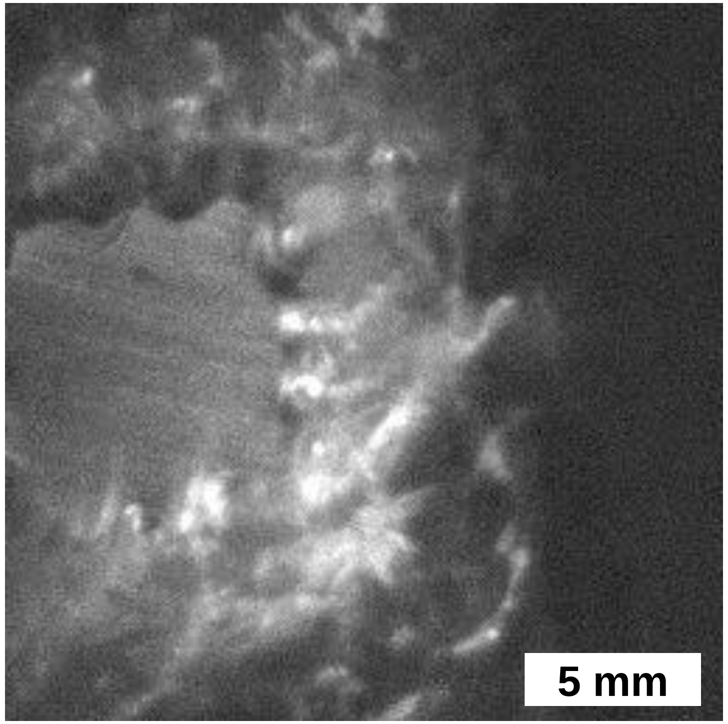
360 V

→ Very fast and high hydrodynamic process

Understanding Pep Developement of VGE

High-speed Camera recordings starting submerged: 0.0 ms ≤ t ≤ 8.33 ms

→ t = 3.17 ms



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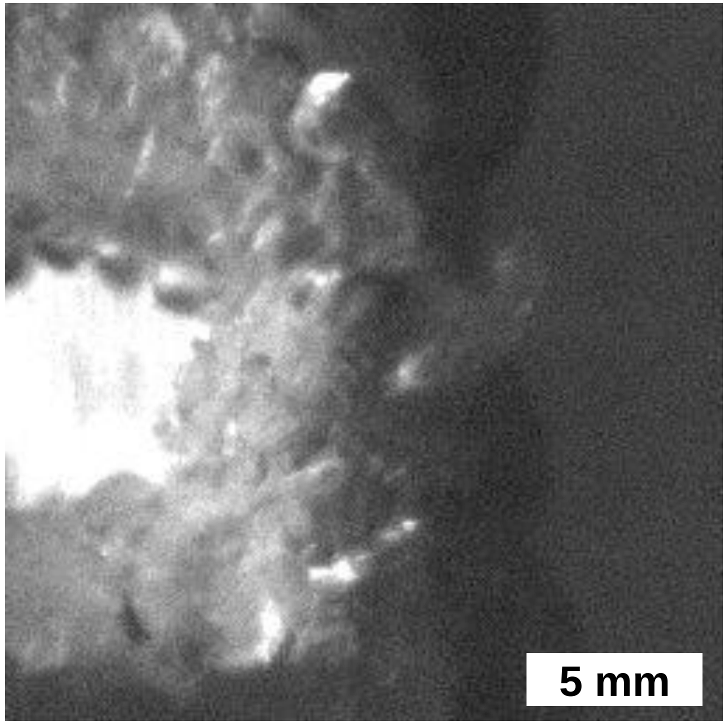
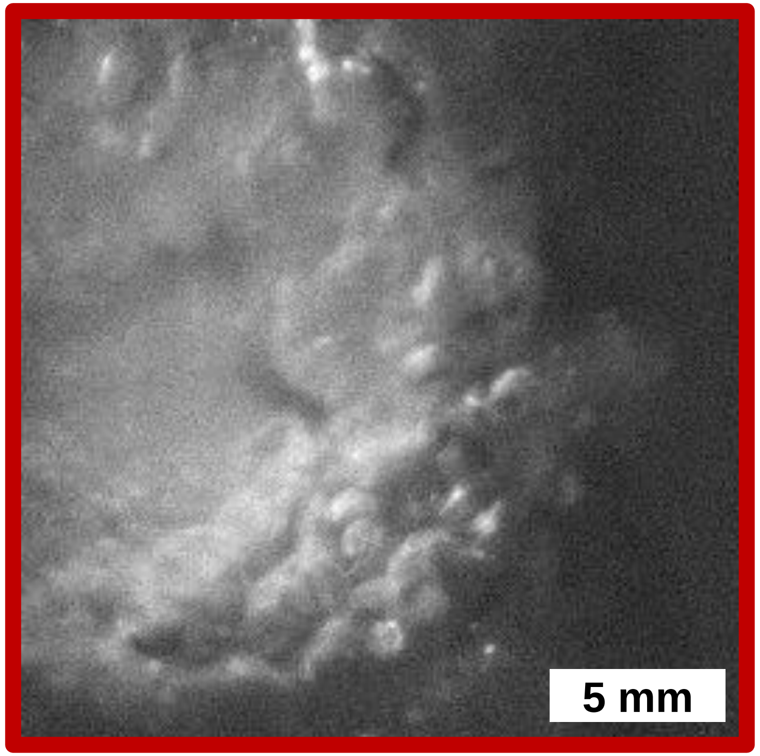


340 V



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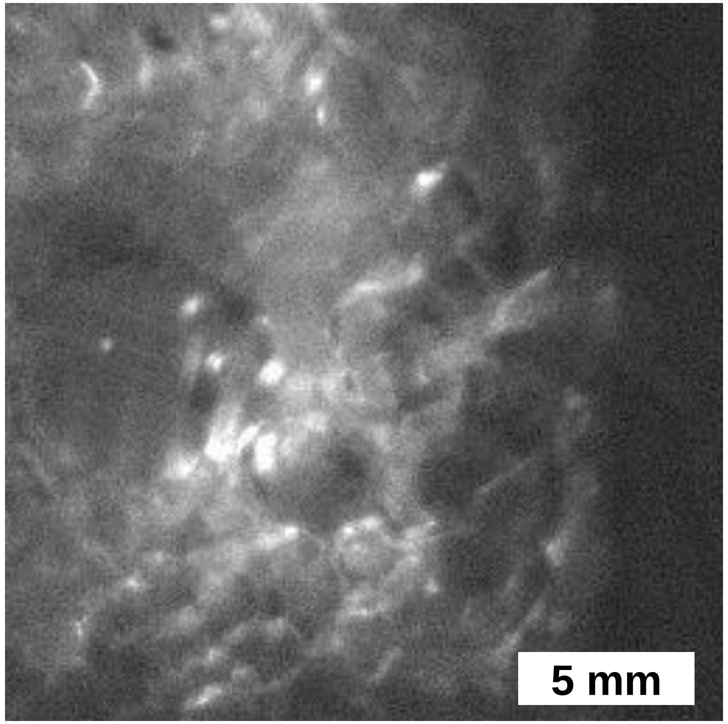
→ Very fast and high hydrodynamic process

Understanding Pep

Developement of VGE

High-speed Camera recordings starting submerged: 0.0 ms ≤ t ≤ 8.33 ms

→ t = 4.17 ms



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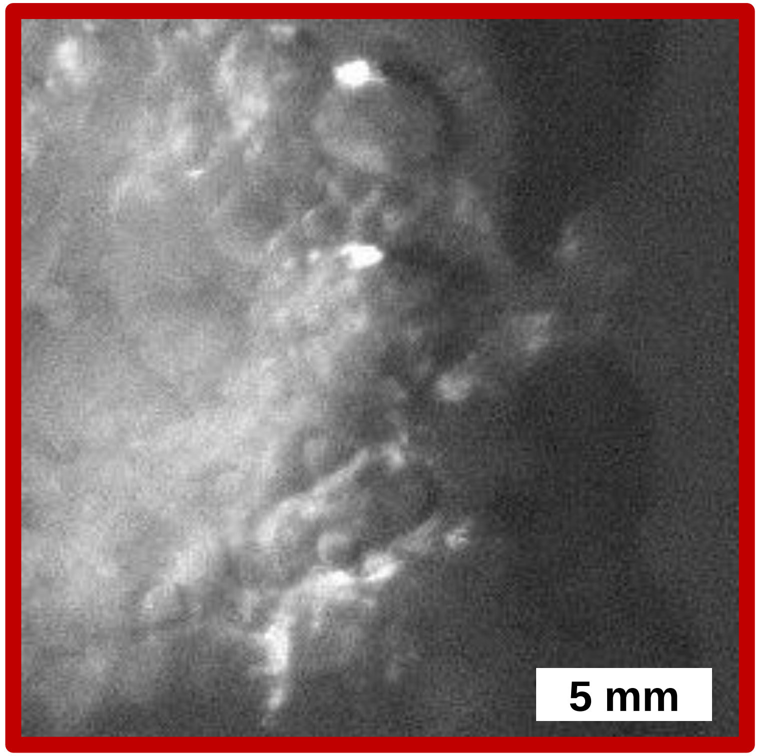

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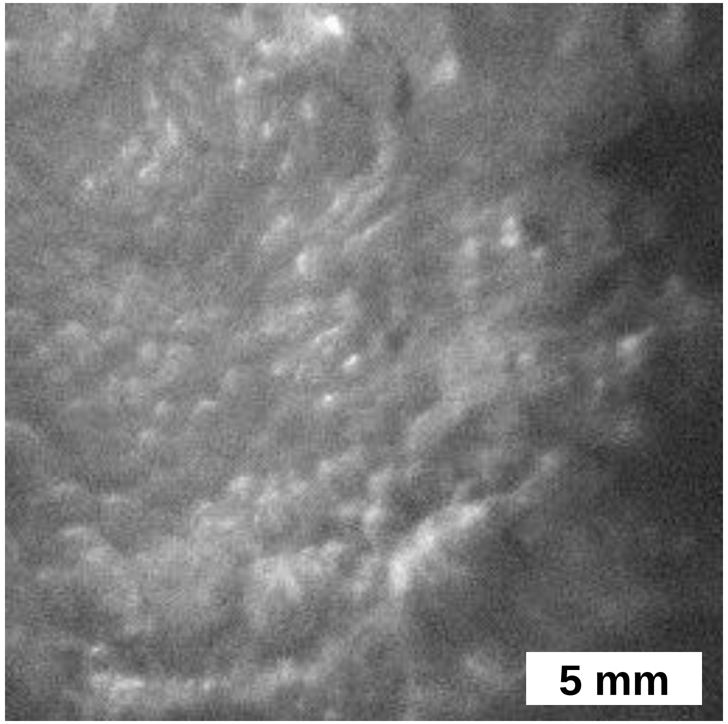

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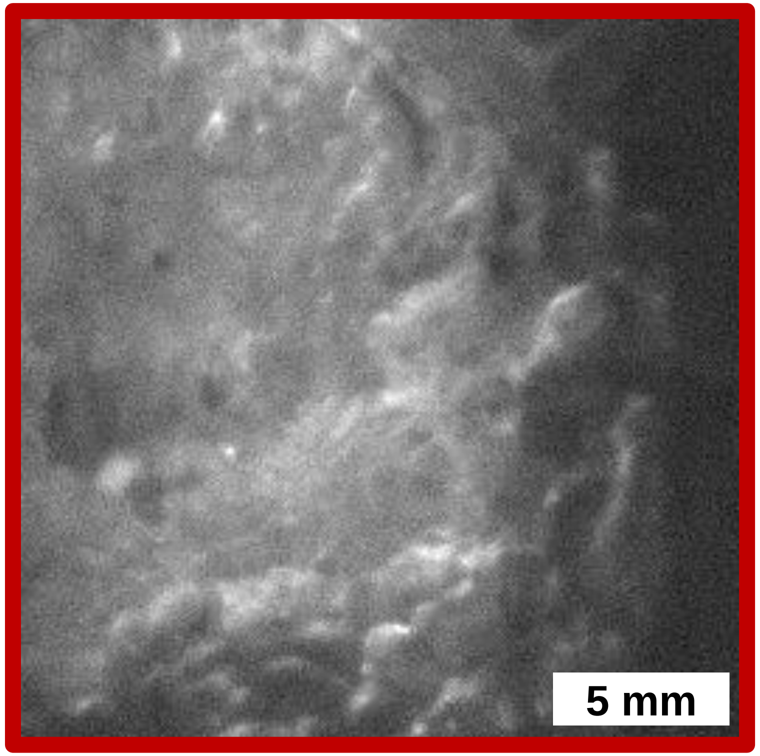
→ Very fast and high hydrodynamic process

Understanding Pep

Developement of VGE

High-speed Camera recordings starting submerged: 0.0 ms ≤ t ≤ 8.33 ms

→ t = 5.00 ms



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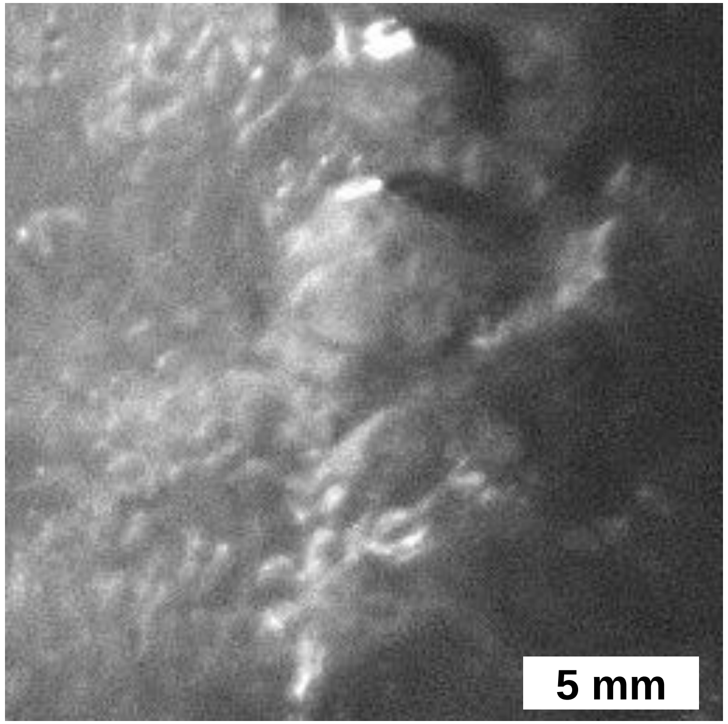

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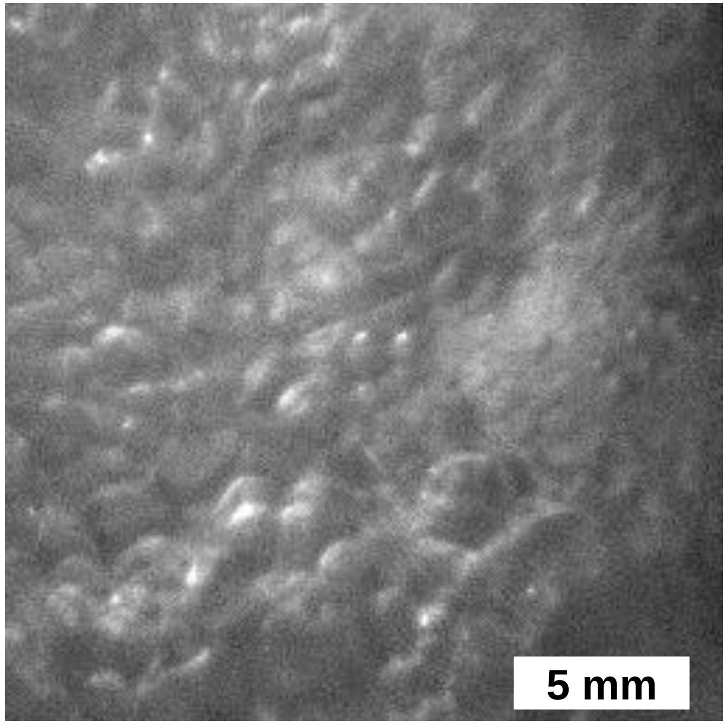
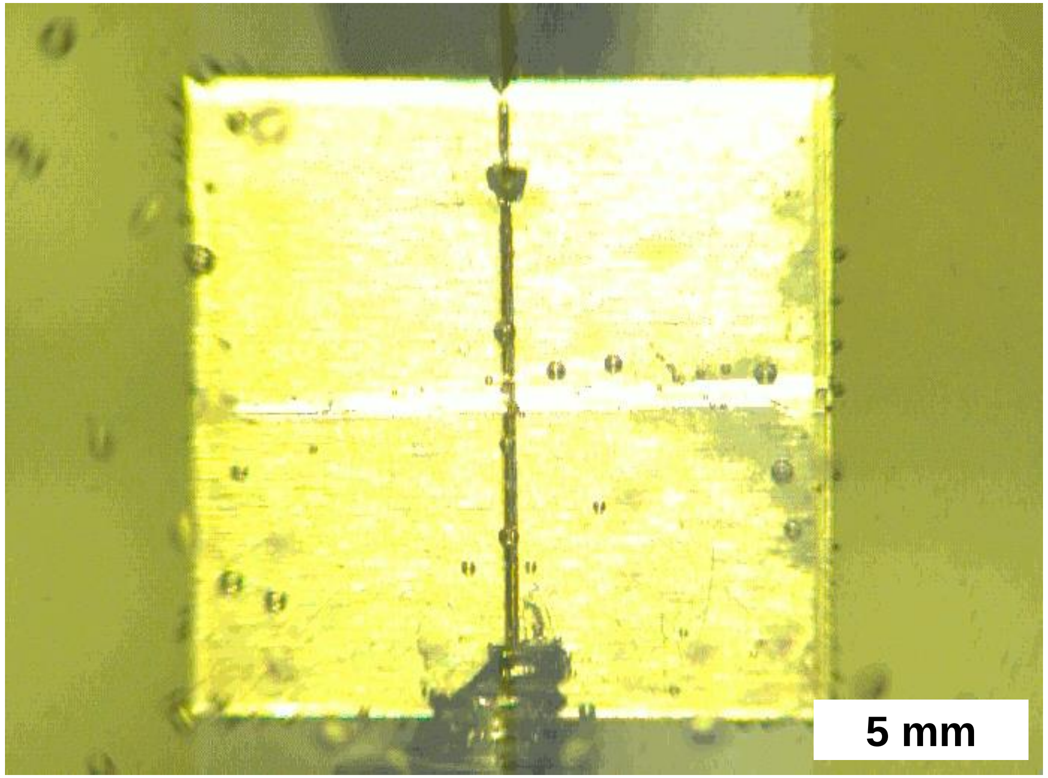


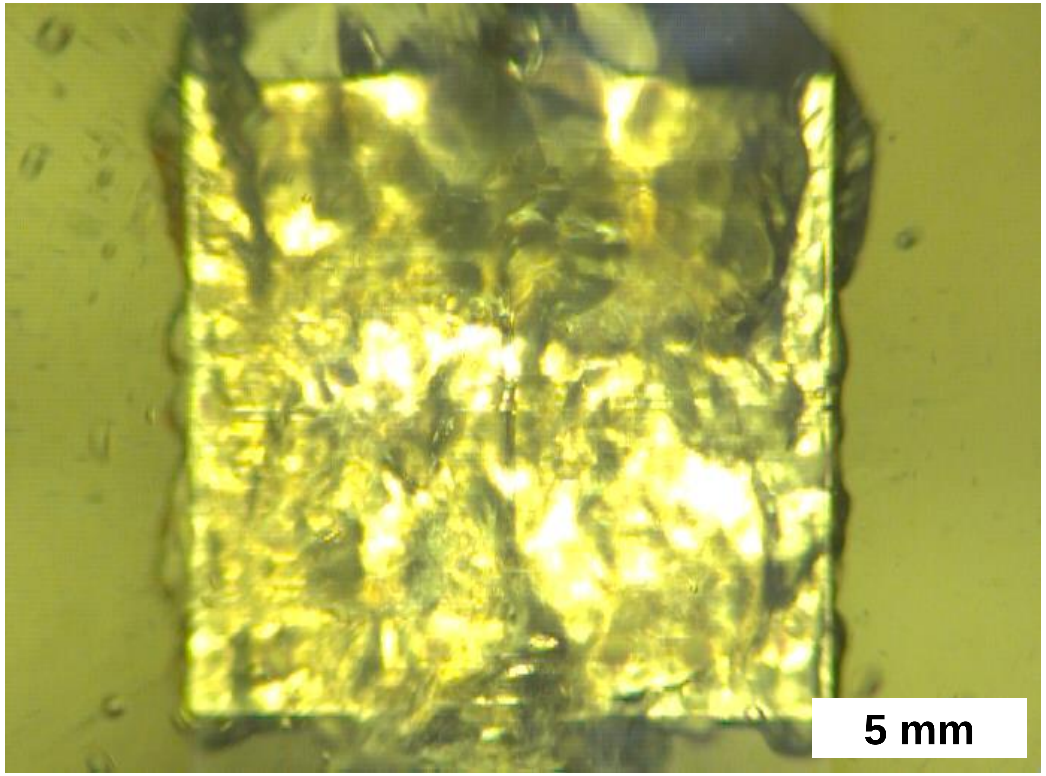
360 V

→ Very fast and high hydrodynamic process

Understanding Pep stable process and continuose VGE



Understanding Pep stable process and continuose VGE



continuose: → allover (vs. lokal breakdowns)

→ development

\+

growing/merging

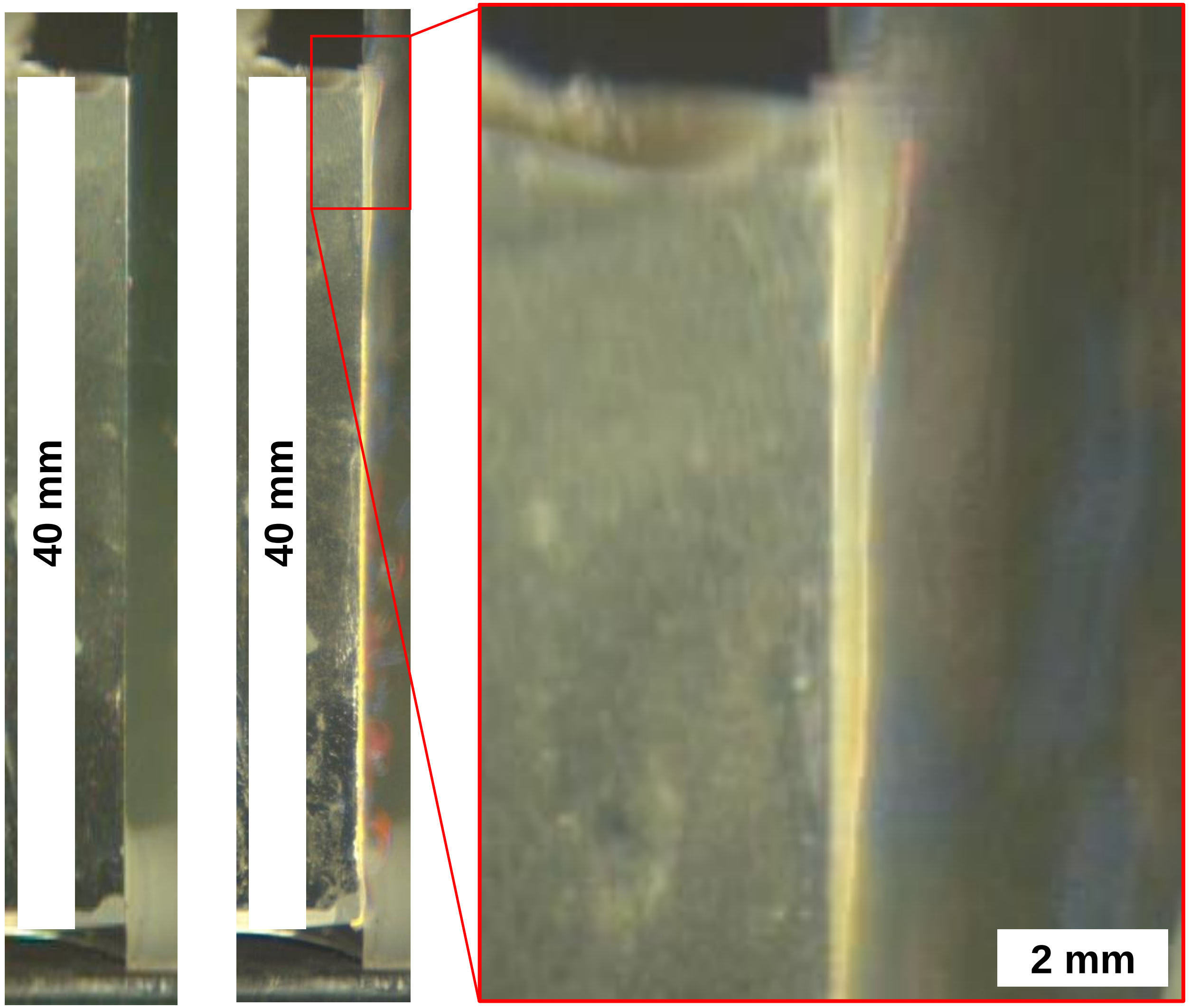
\+

upraising and releasing from sample

… and

pulsating: → (lokal) thickness changes dynamically

Understanding Pep VGE conditions over heigh



„cross section“ of VGE / plasma region:

→ sum up of vape/gas from bottom to top

→ <u>(average) thickness grows from bottom to top</u>

non-uniform conditions:

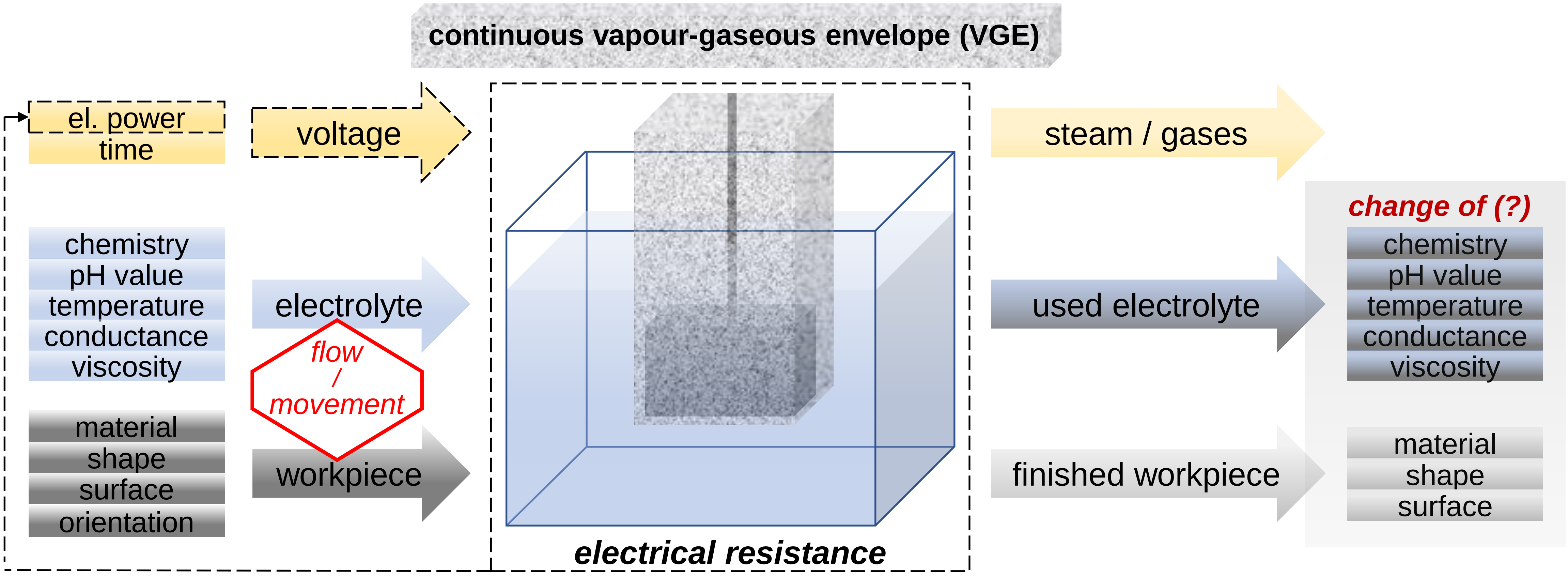
→ **stronger material remove rate (MRR) and**

→ **higher gloss**

down(side) than up(side)

Understanding Pep

effect of electrolyt flow on VGE



continuous vapour-gaseous envelope (VGE)

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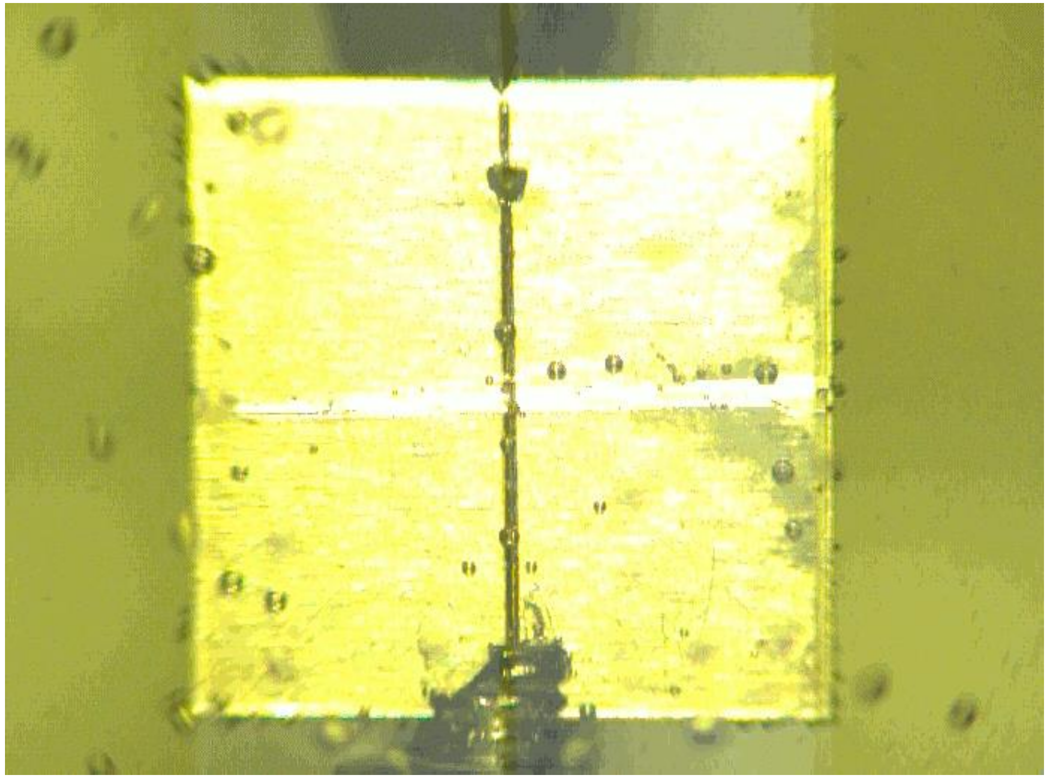
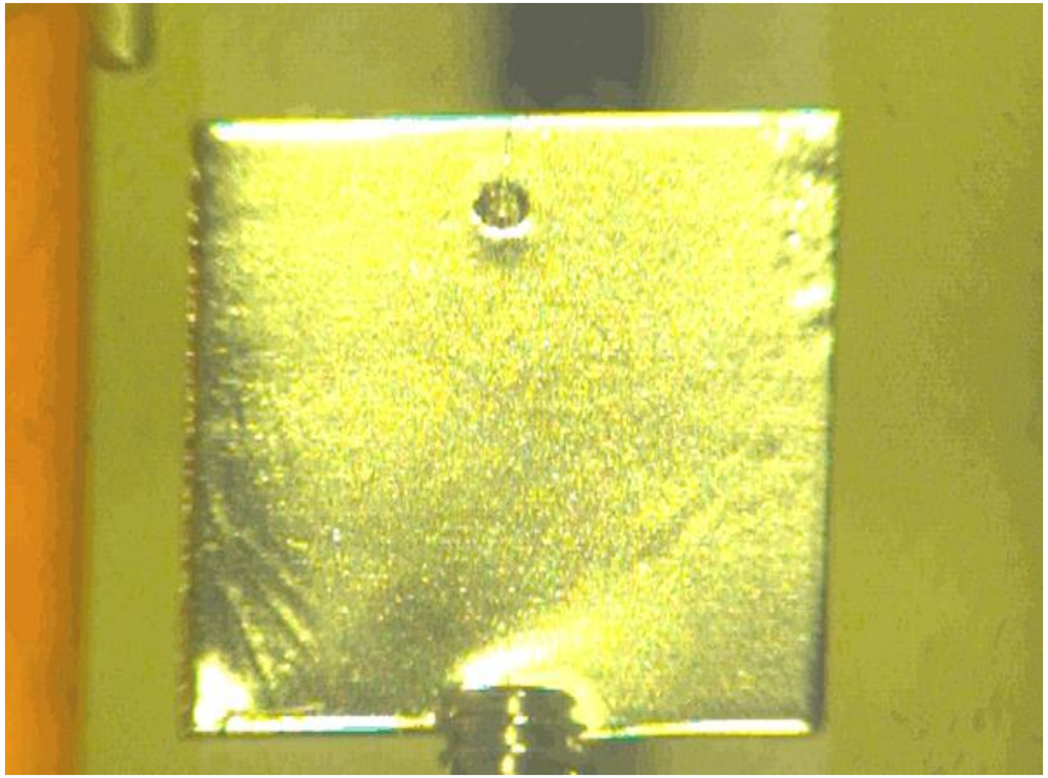
Understanding Pep effect of electrolyt flow on VGE

no additional flow: 0 m/s

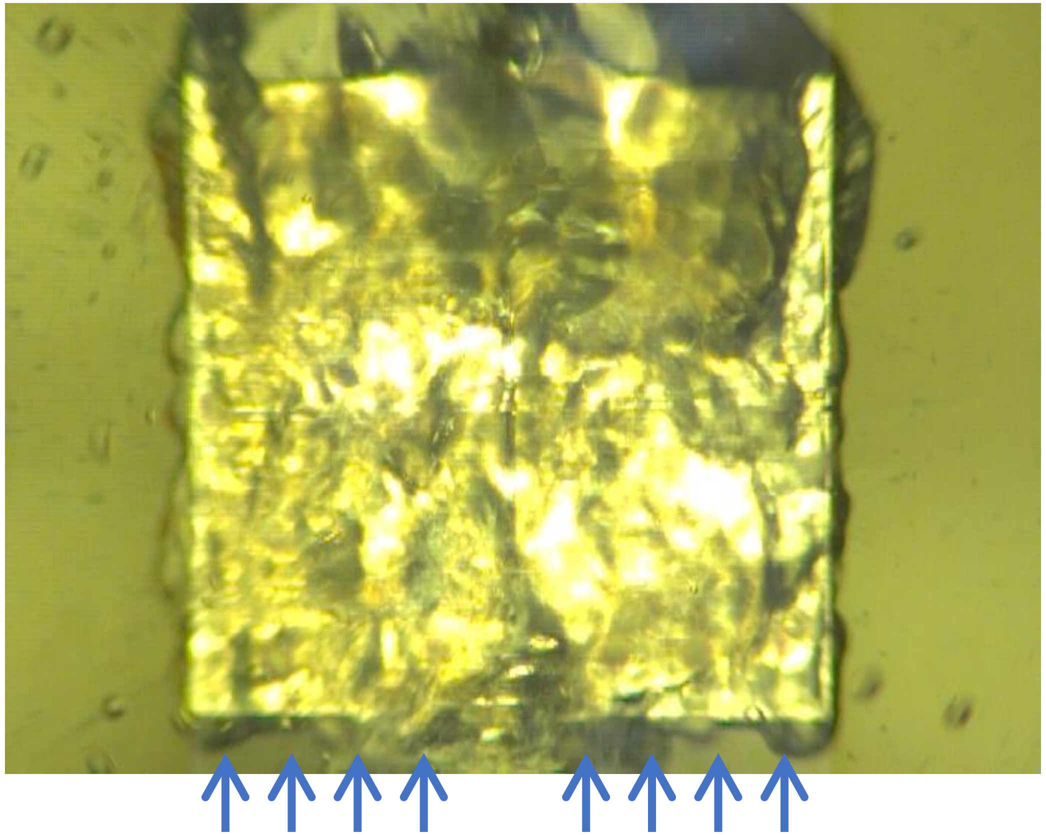


additional flow (from left): 1.2 m/s



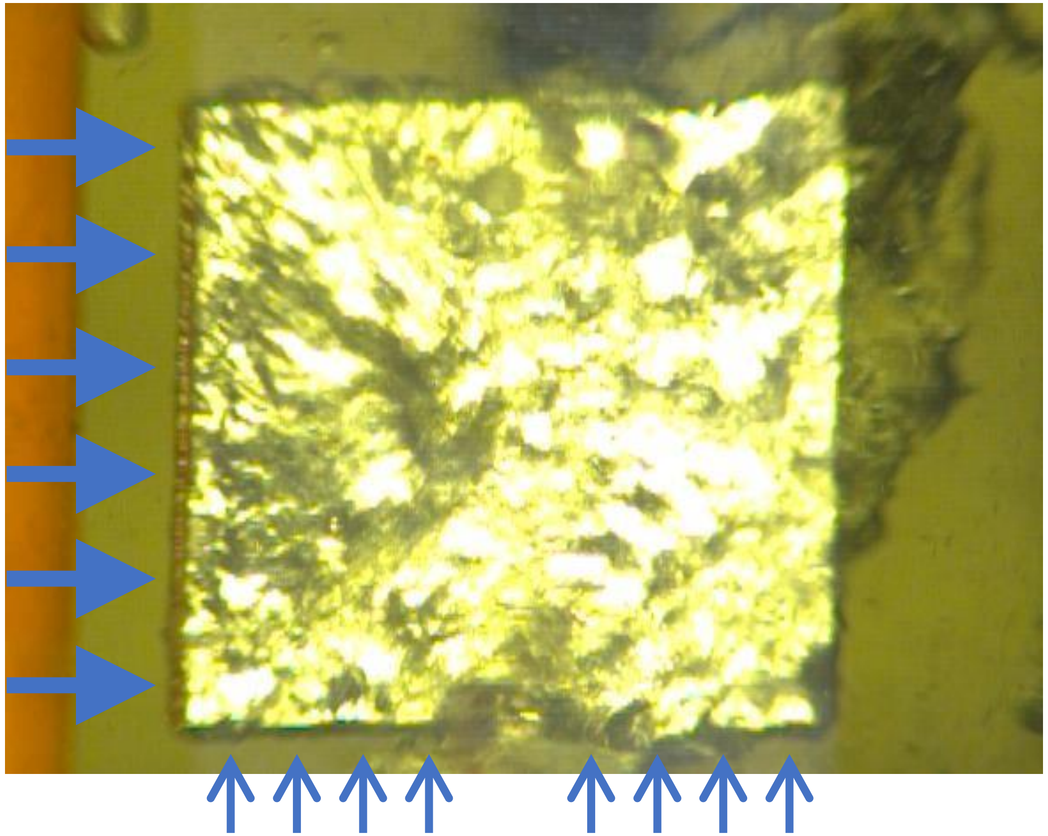
Understanding Pep — effect of electrolyt flow on VGE

no additional flow: 0 m/s



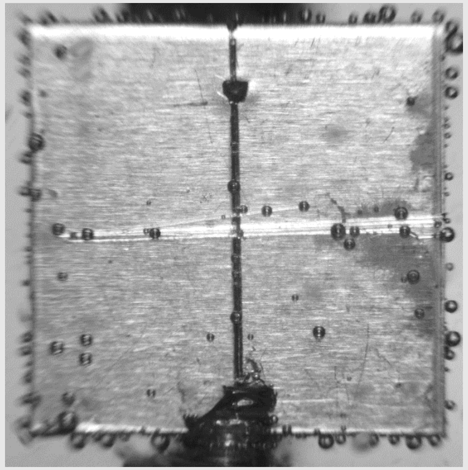
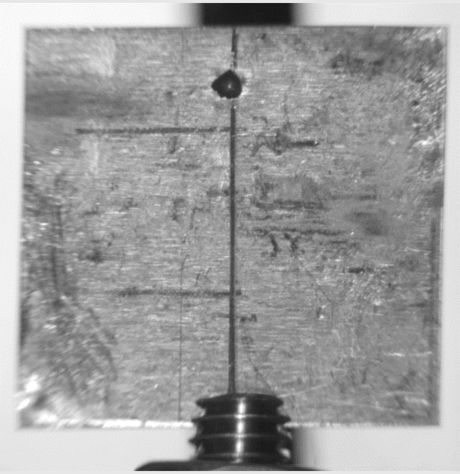
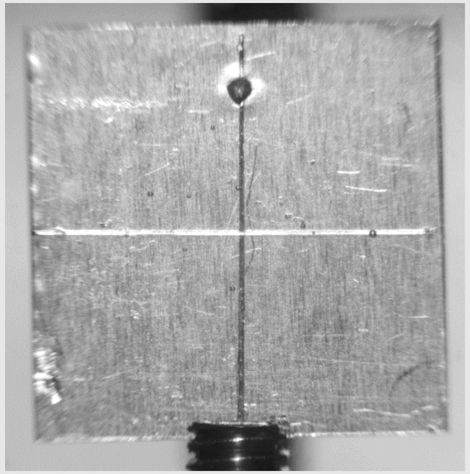
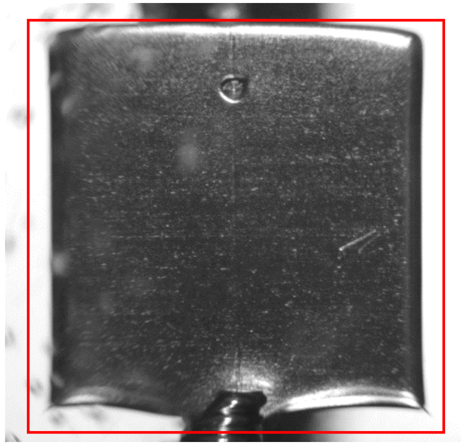
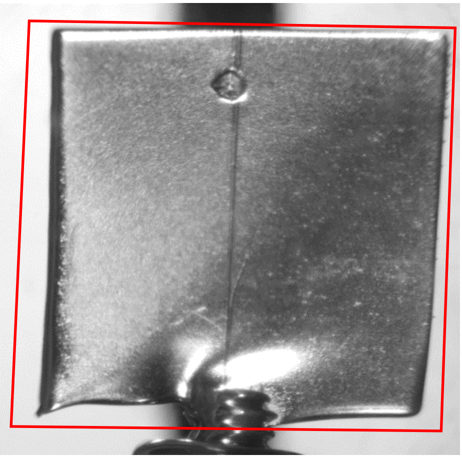
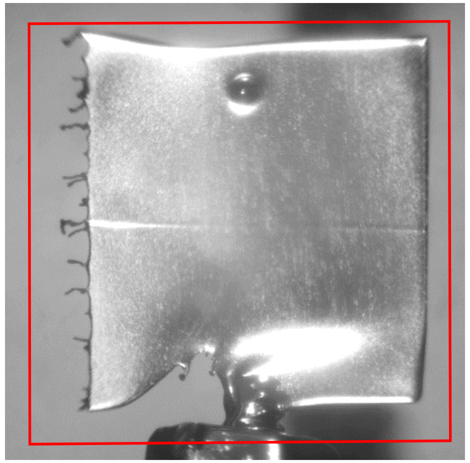
“natural” electrolyte streaming

additional flow (from left): 1.2 m/s



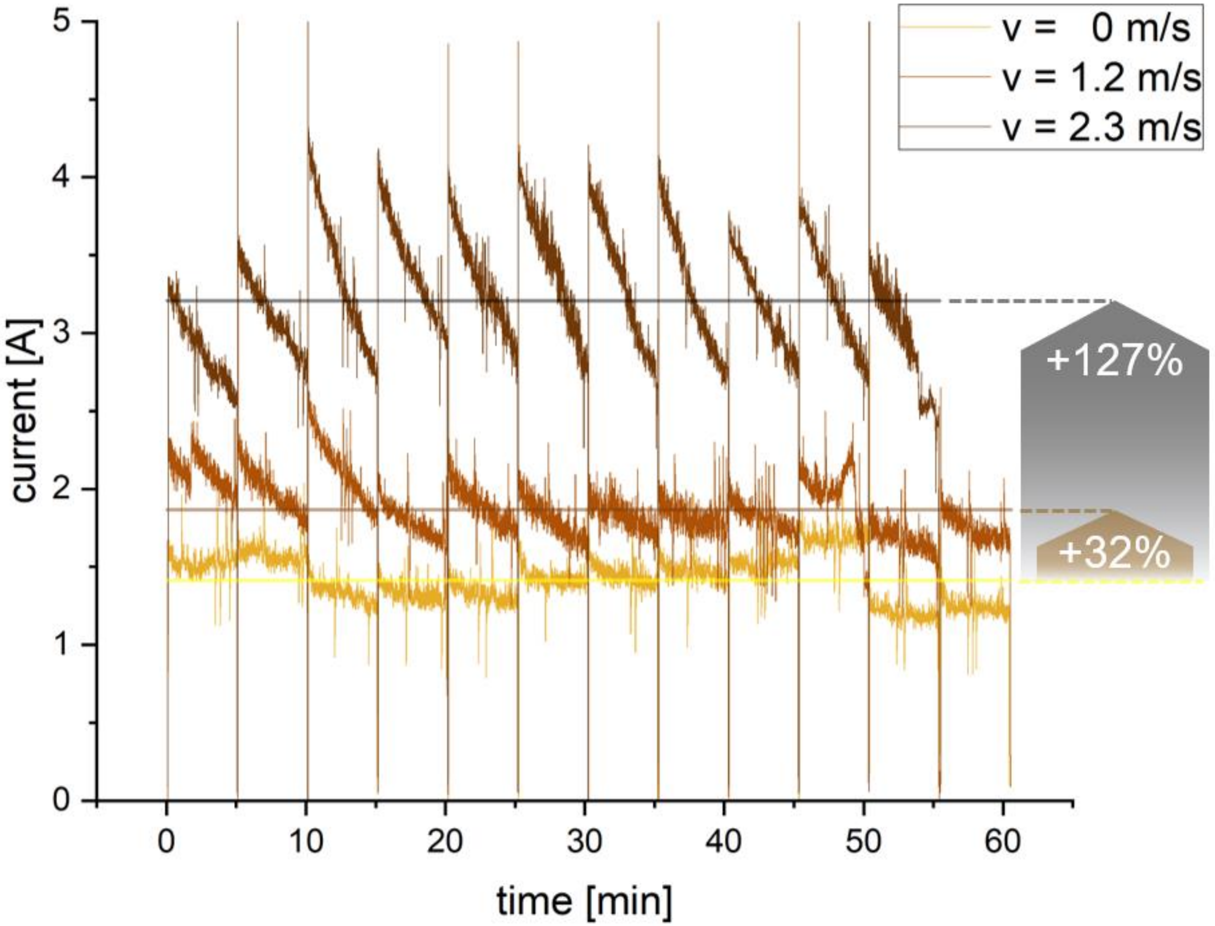
Understanding Pep

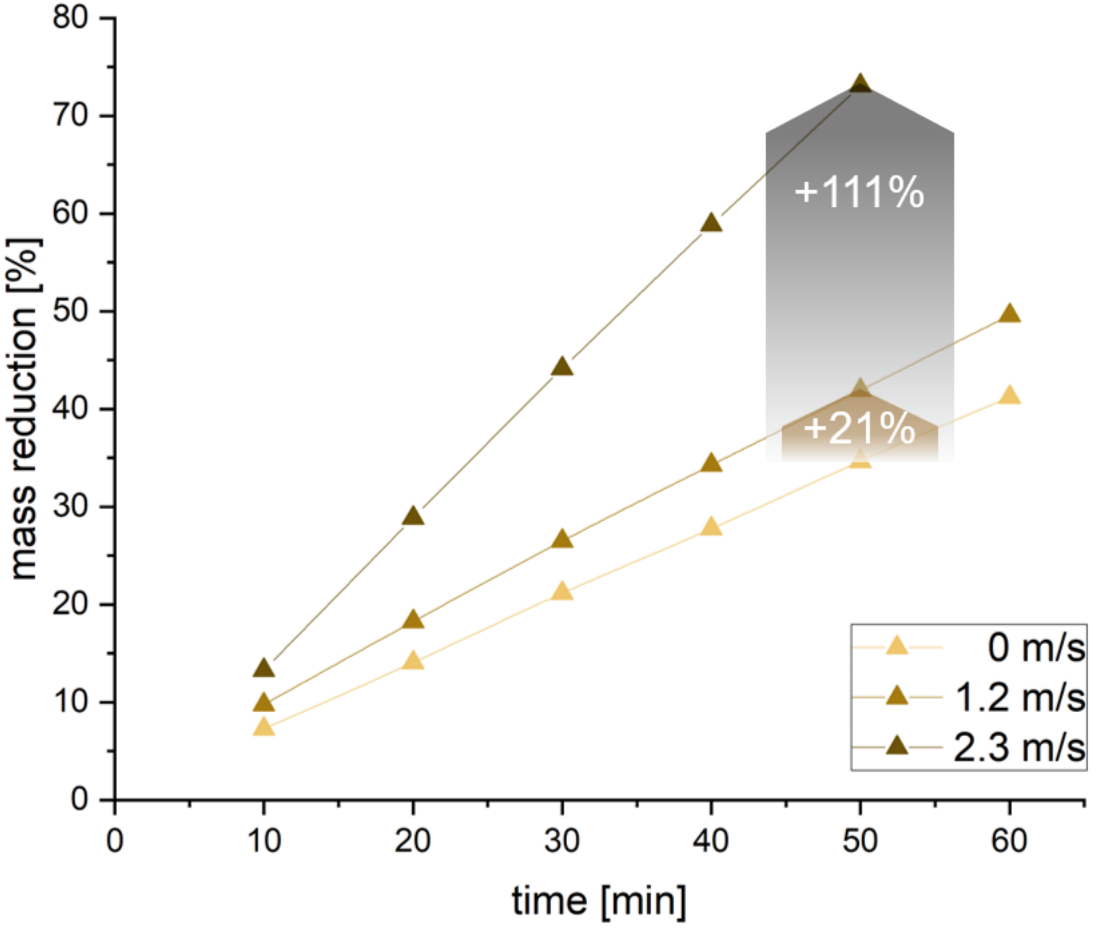
effect of electrolyt flow on VGE

	0 m/s	1.2 m/s	2.3 m/s
0 min			
40 min			

Understanding Pep

effect of electrolyt flow on VGE

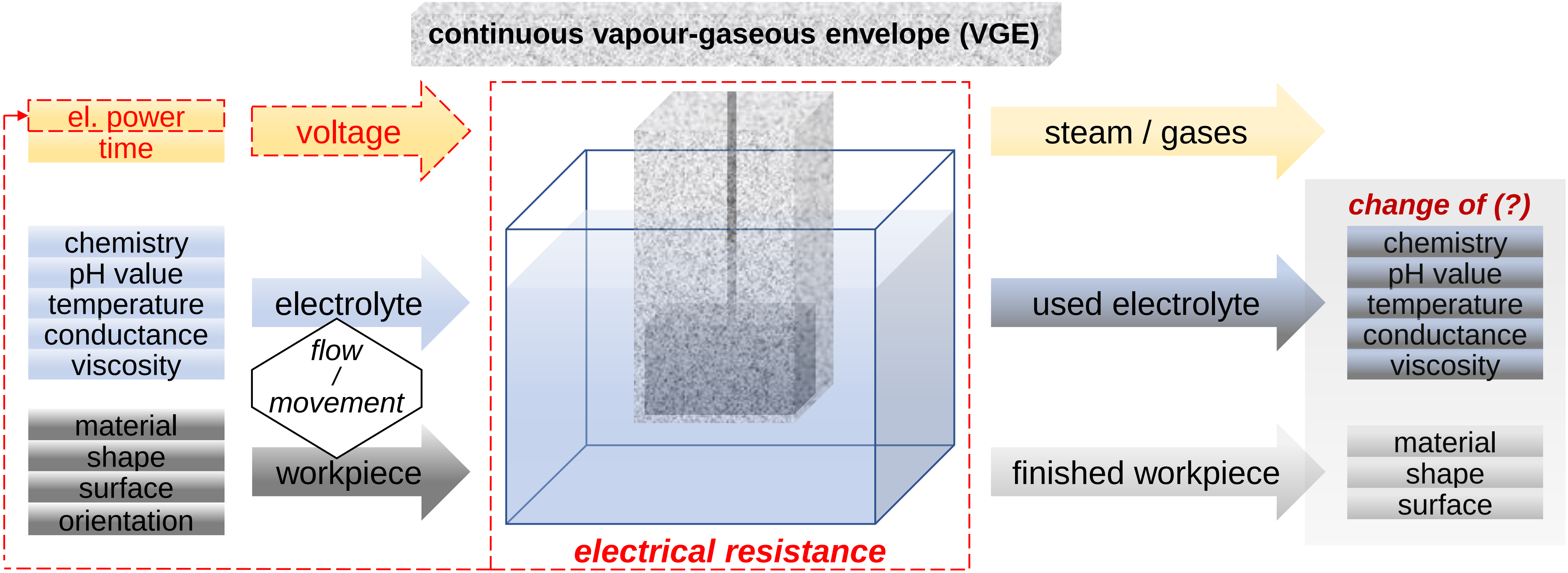




additional flow of electrolyte increase current density and material removal

→ *Relative movement surface – electrolyte:* very strong effect on PeP-results!

Understanding Pep energy



continuous vapour-gaseous envelope (VGE)

el. power
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Understanding Pep energy

energy conservation law:

energy conservation law:	E_{input}	=	E_{output}
	E(electrical + thermal + chemical)	=	E(~~electrical~~ + thermal + chemical)

If the chemistry of the electrolyte has the opportunity to dissolve the workpiece material, a part of the input **electrical charge** will lead to the oxidation of the anodic workpiece (= material removal).

If not, it is mainly a **change of electric into thermal energy** (material removal and/or surface smoothening could be possible by local melting/evaporating of metal).

electrical charges (current I) = main drivers of PeP

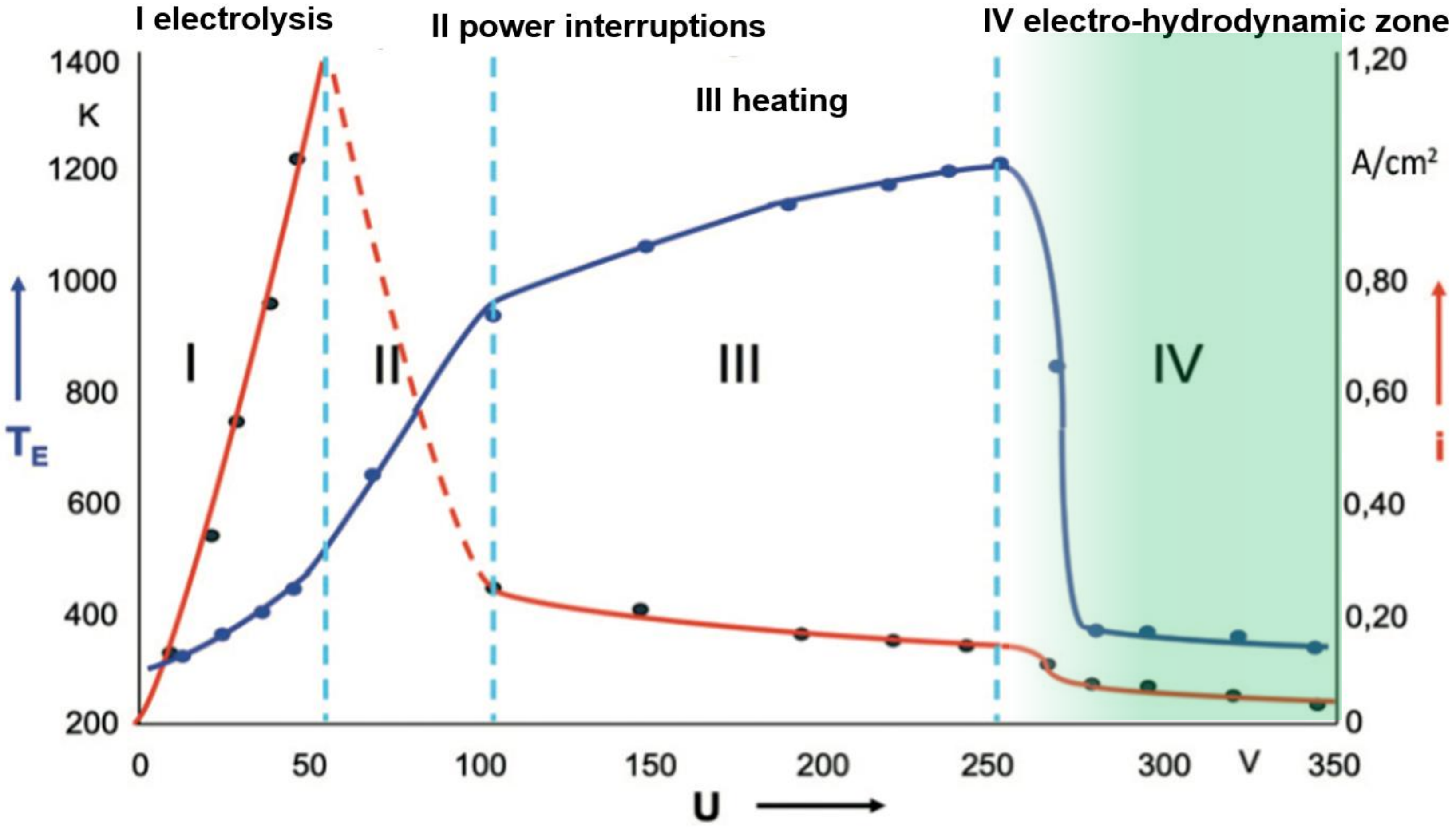
+

voltage range (U = ~280 to ~370 V) for material removal AND high surface finish

Understanding Pep

lower voltage limit

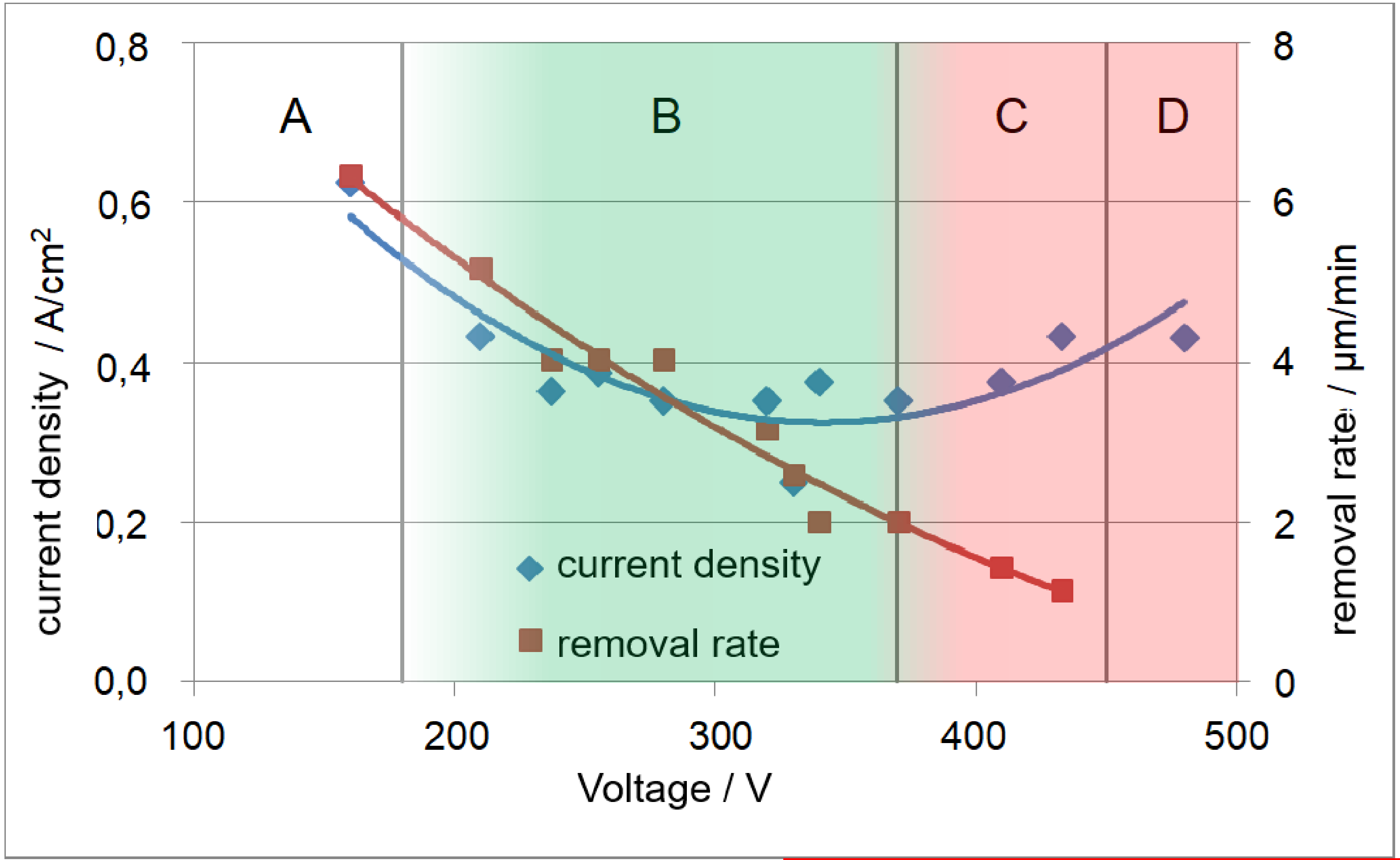
inside electro-hydrodynamic zone: VGE leads to high thermal isolation (→ $T_{workpiece}$ = ~100 °C) and electrical isolation (high voltage drop → ionisation / plasma)



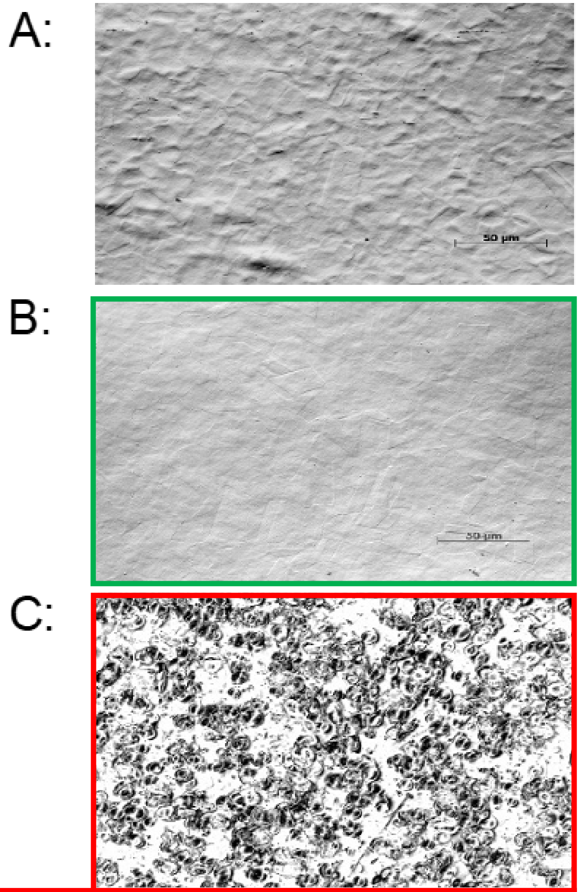
voltage limit shifted up or down, depending on resistance of system

Understanding Pep

upper voltage limit



surface topology

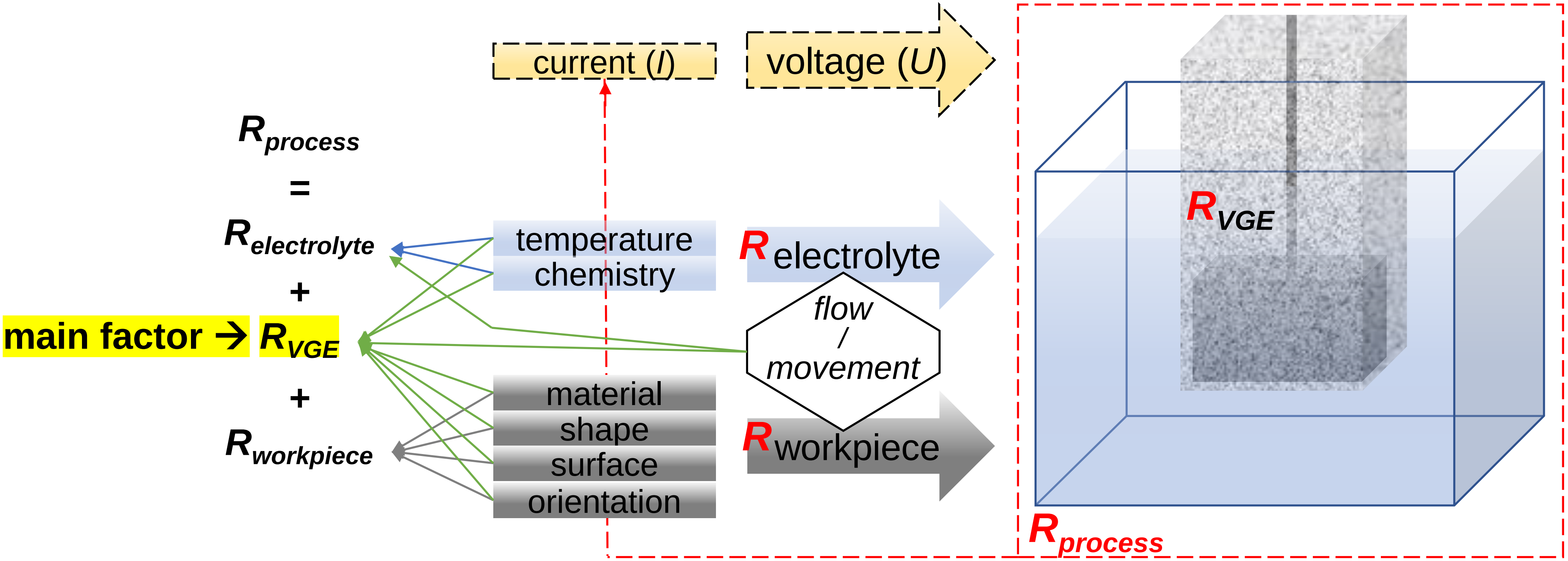


A – no stable plasma
B – homogeneous plasma

C – glow- and spark discharge
D – spark discharge

Avoid! → craters

Understanding Pep electrical resistance and current



current (I)

voltage (U)

$R_{process}$

=

$R_{electrolyte}$

+

main factor → R_{VGE}

+

$R_{workpiece}$

temperature
chemistry

material
shape
surface
orientation

R electrolyte

flow / movement

R workpiece

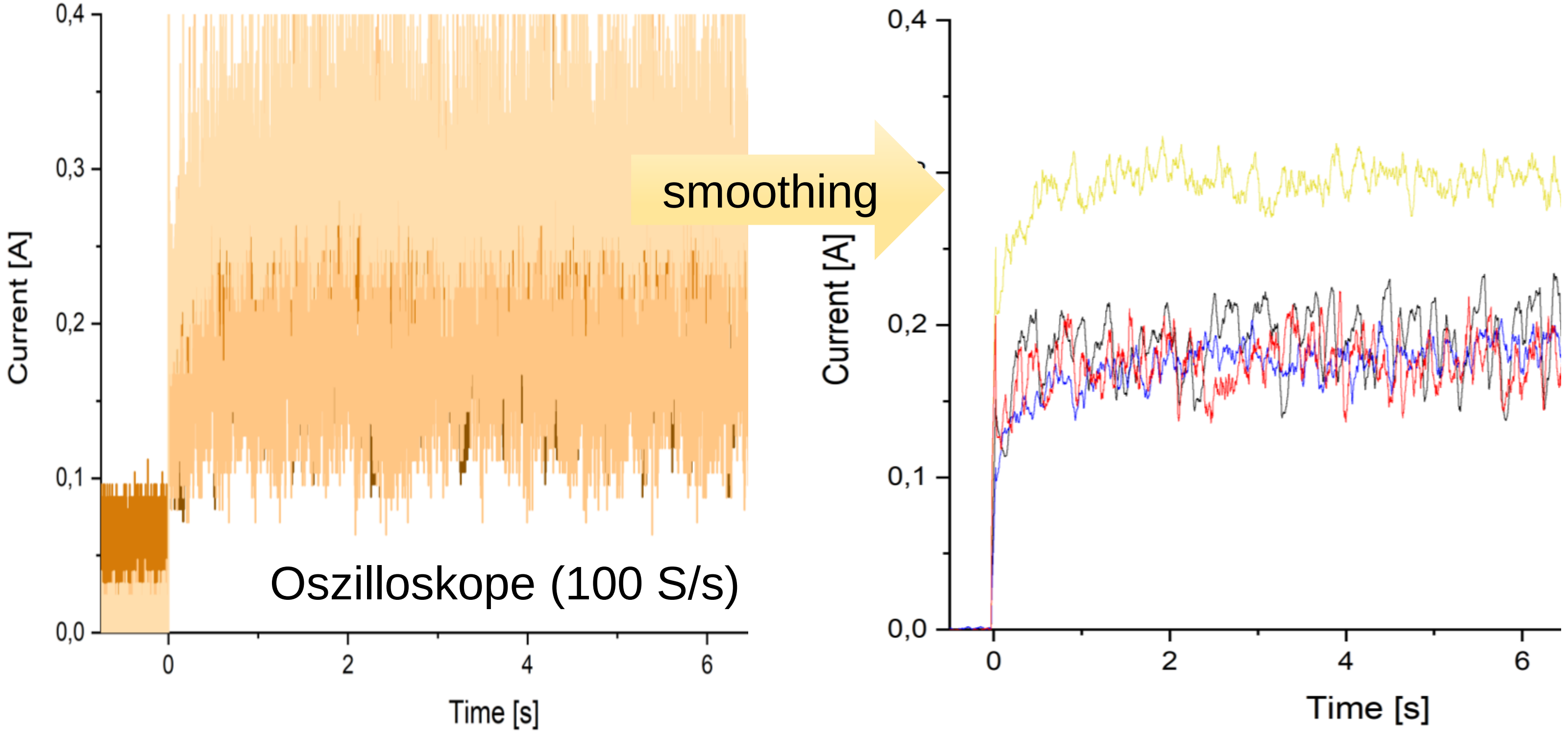
R_{VGE}

$R_{process}$

→ **Ohm‘s law:** $I = U / R_{process}$ the resulting current(flow) is the main driver of the PeP-process (and also the main live-value/parameter to characterise the process)

→ **Amount of charge** $Q(t) = \int I(t)dt$ most important/correct parameter on the input-side to describe “how much PeP” was done

Understanding Pep measurement current/charge



PeP is a highly dynamic process: 10^3 to 10^x? current jumps/second with large amplitudes

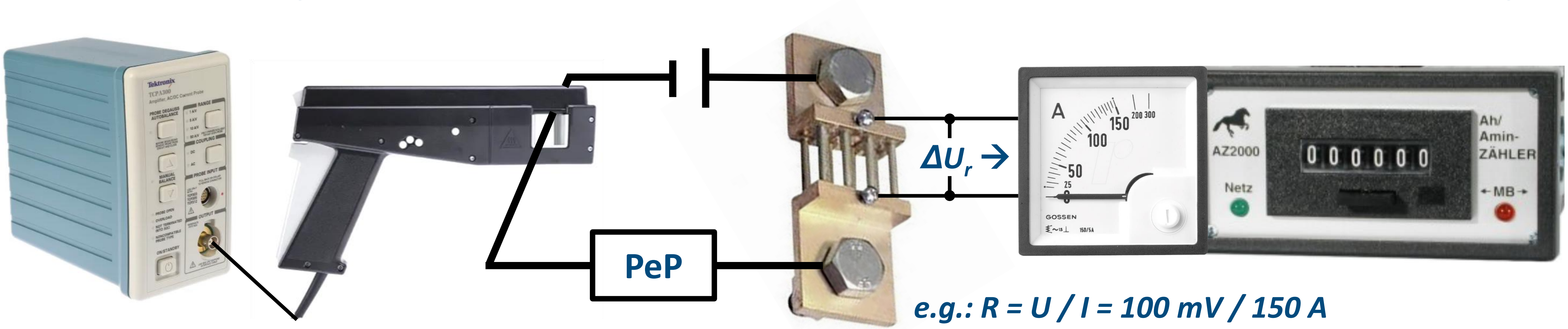
→ most exact measurement by oszilloskop, but: hard to read and lot of data → need of smoothing

→ digital displays: live values not good to read (fast changing)

→ physical needle analog meter (slugish behaviour = smoothing): good and simple to read

Understanding Pep

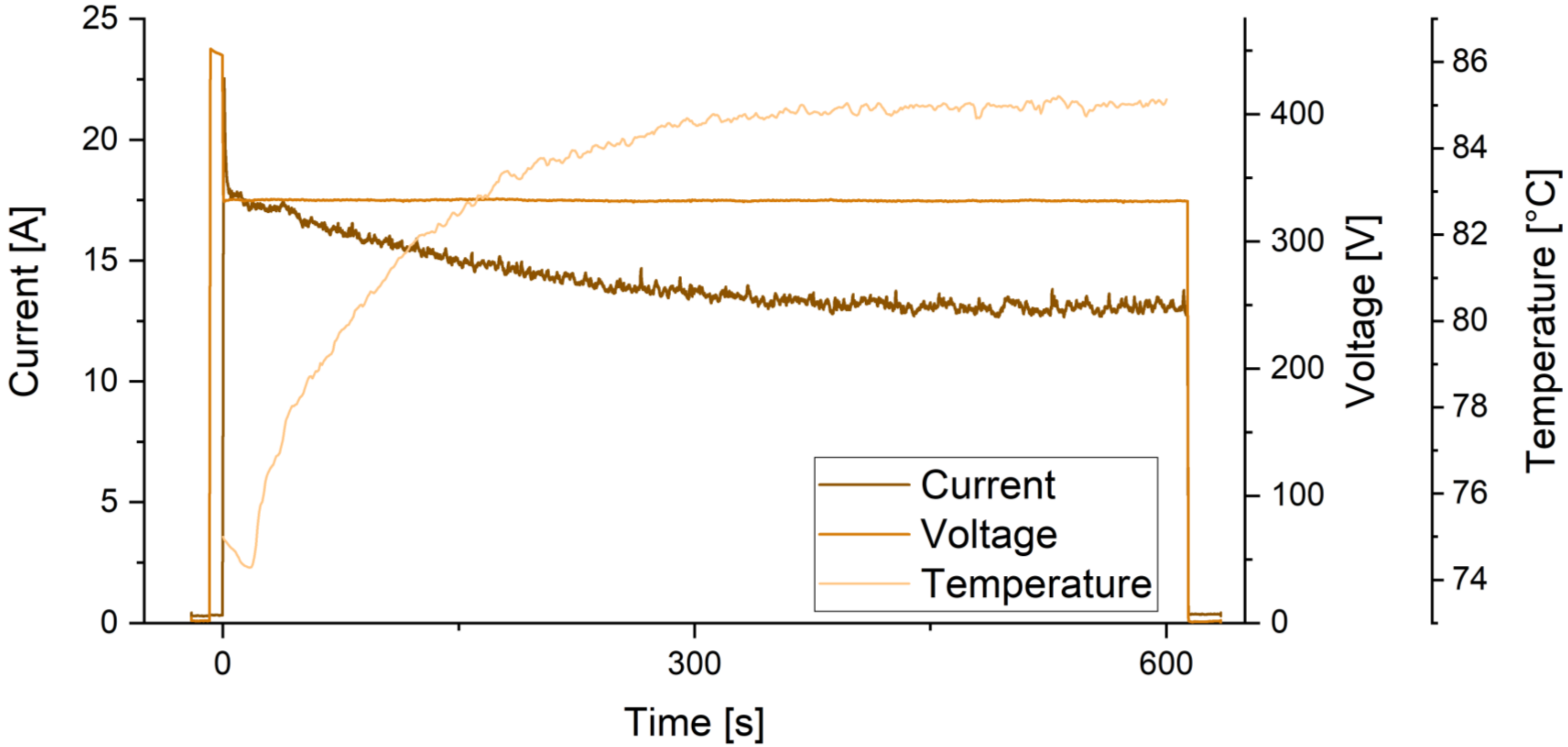
measurement of current/ charge



e.g.: R = U / I = 100 mV / 150 A

	current probe + amplifier	shunt	charge integrator
principle	magnetic field of cable + Hall effect	voltage drop of a defined resistor (I = U / R)	voltage drop of **shunt** → integrating current over time
advantages	current circuit not affected contactless easy to use and safe	high accuracy (also current spikes) direct measurement cost-effective	easy to read cost-effective
dis-advantages	less accuracy at low current sensitiv to magnetic fields over range spices problematic expensive	circuit interuption → (small) voltage drop	

Understanding Pep current and temperatur



- current spike due to fast immersion of the part and formation of VGE
- continuos drop of current due to increasing temperature and smoothing of surface and so decreasing the real surface area

Understanding Pep current and temperatur

I = U / R and U is constant

→ when measured current is lower at higher tempertures then the (total) resistance must be higher

- higher temperatur of workpiece: → higher resistance
- higher temperature of electrolyte: → higher mobility of ions → lower resistance *but*
  → thicker VGE (?) → higher resistance

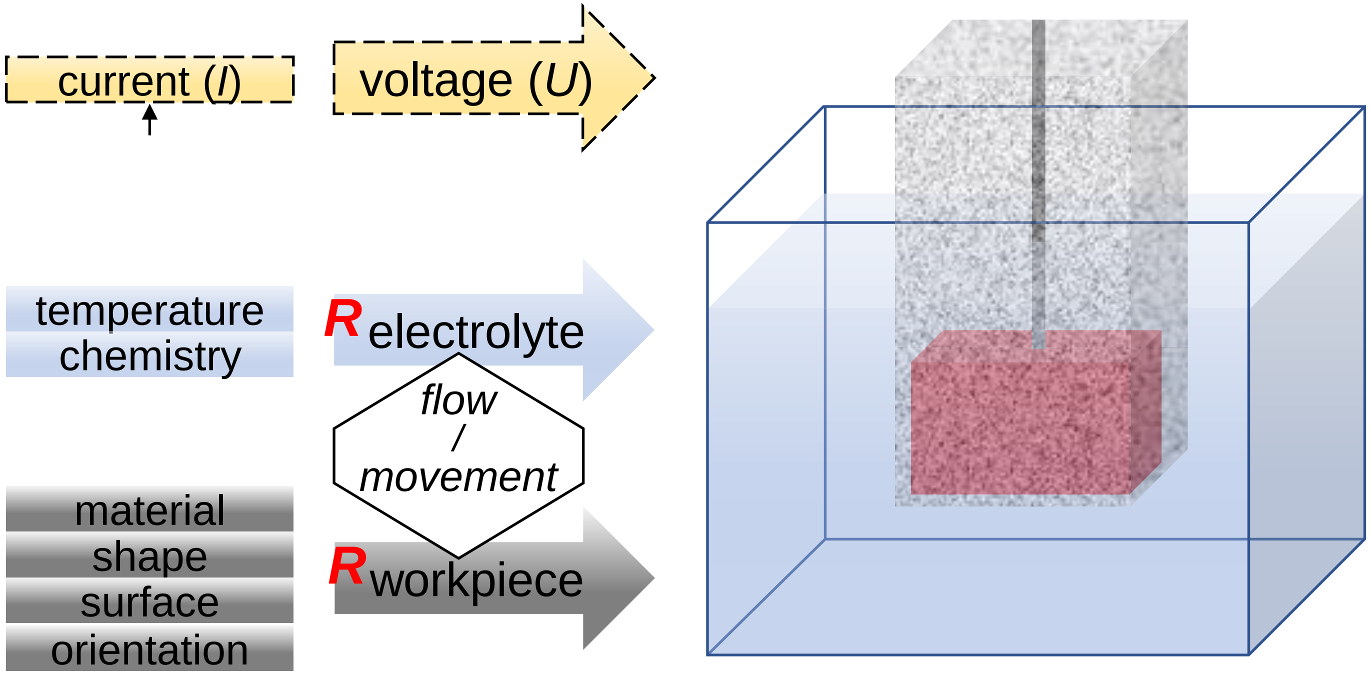
I = U / R and U is increased

→ current should be higher but there is no clear effect to see (compare to slide: upper voltage limit)

- higher voltage can influence chemical, physical and plasma processes so that the recistance is also increased and in total the current not increases

Understanding Pep

current density

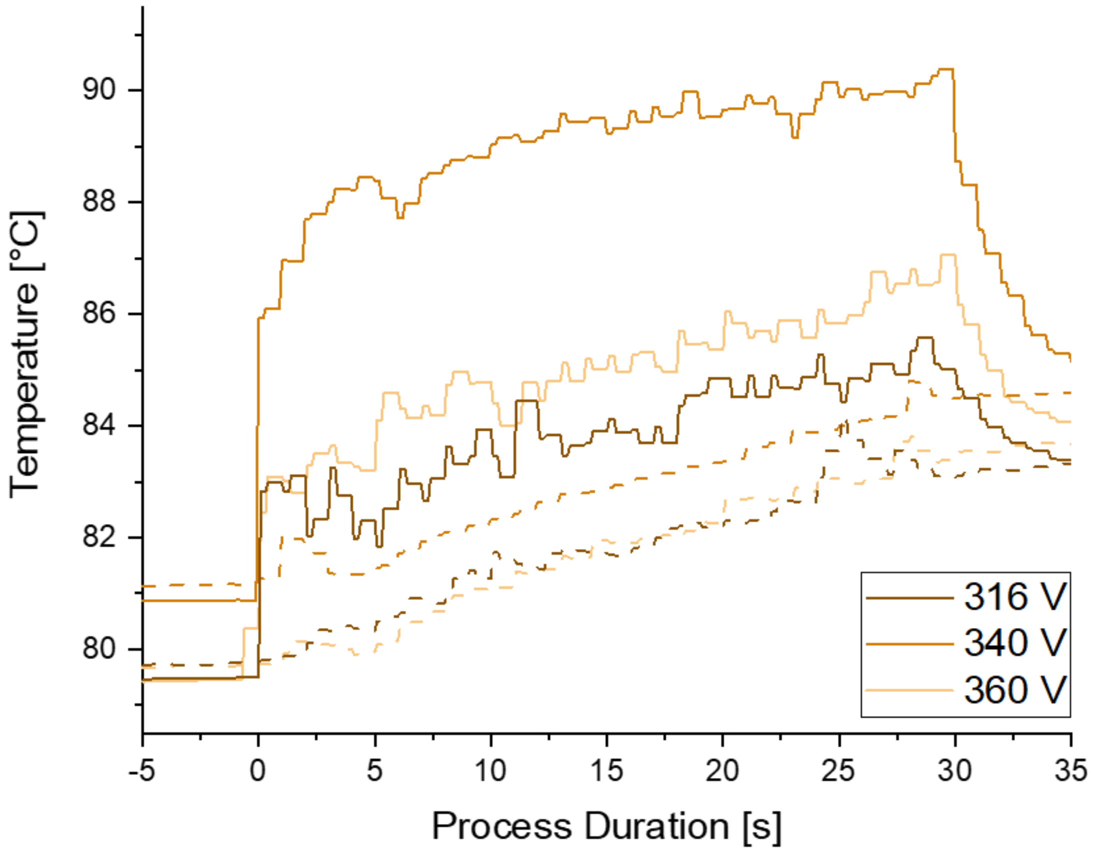


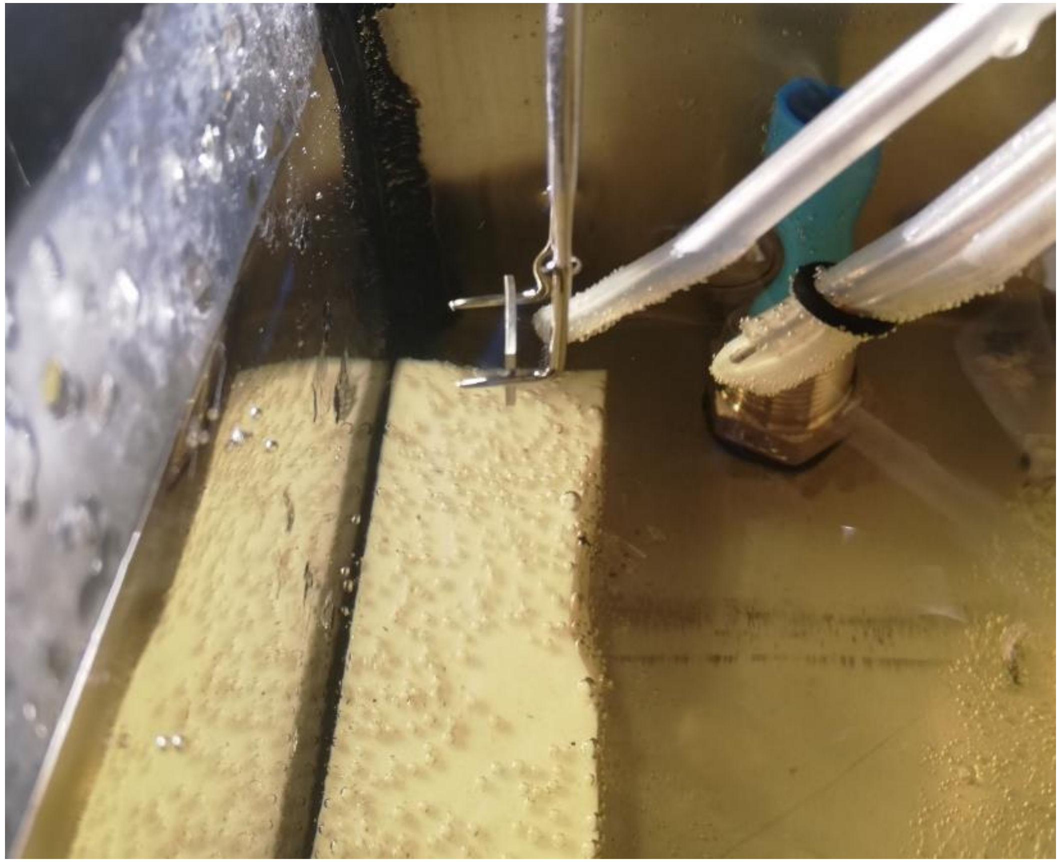
$\vec{J} = I / A_{workpiece}$ …typically given in **A/cm²** is a value, that can describe how intensive the process works on the part

→ mainly affected by the conductivity (chemistry + temperature) of electrolyt and workpiece

→ typicall values: 0.1 – 0.4 A/cm²

Understanding Pep temperature



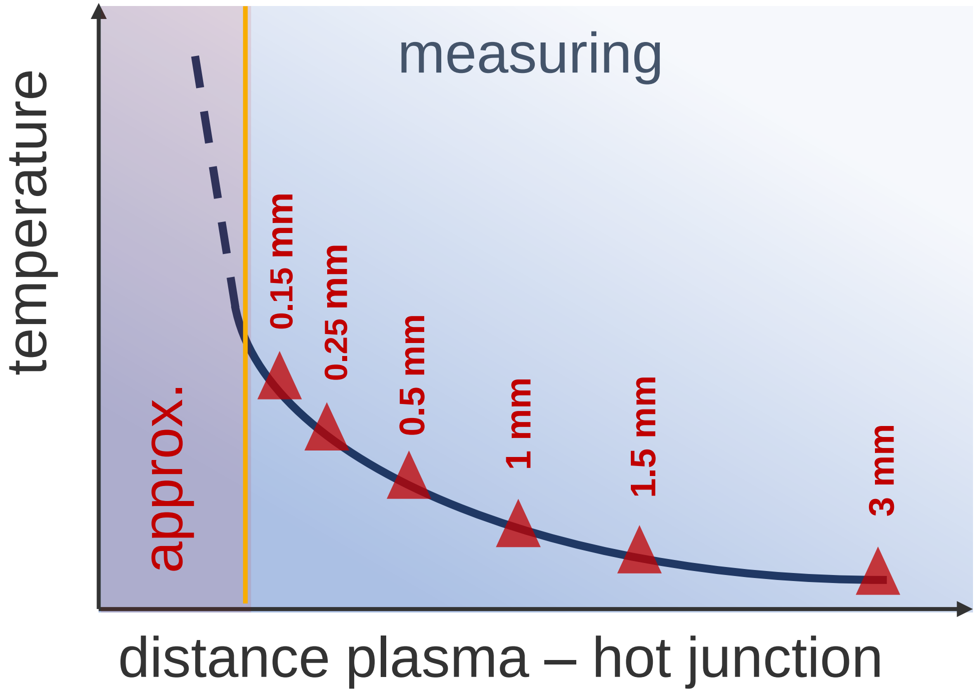


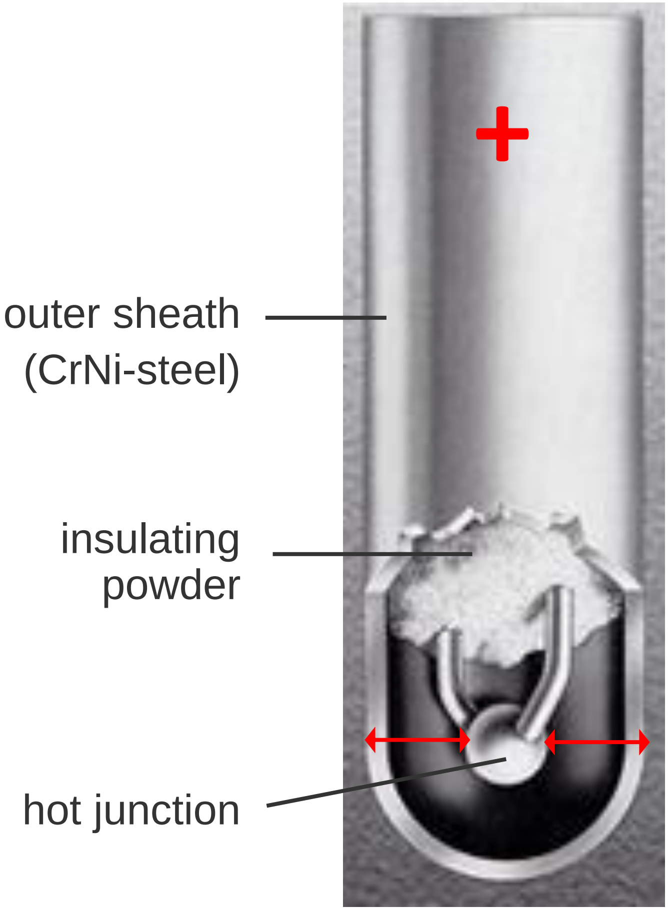
- electrolyte has not „one temperature“, it depends where it is measured

Understanding Pep temperature

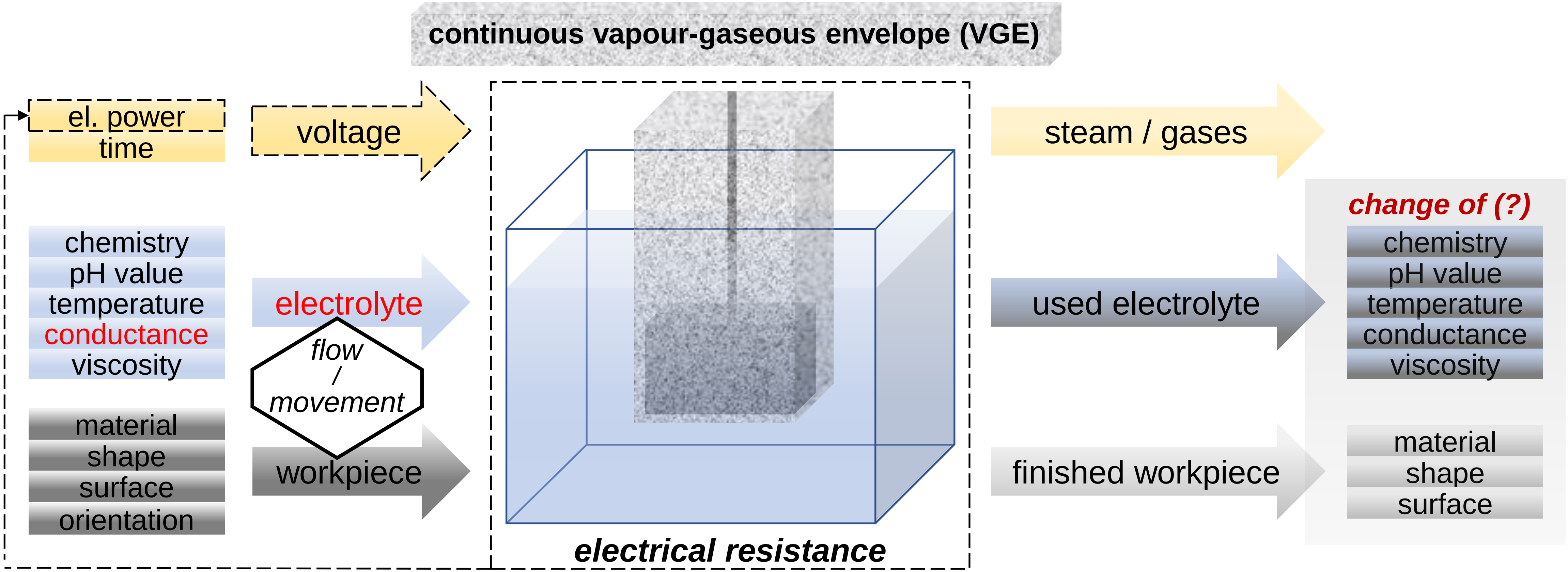
What‘s the temperature of plasma?

Can we measure it with thermocouple?





Understanding Pep conductance of electrolyte solution



- conductivity (κ) of electrolyte mainly influenced by the amount of solved salts/additives and it‘s temperature
- influences total resistance (R) and thickness/stability of VGE: → higher κ → lower R of electrolyte and thinner VGE (also lower R) → higher current → *can* increase material removal, but also surface roughening

Understanding Pep conductance

- conductivity meter with measurement cell with 2 or 4 electrodes
- AC voltage applied across electrodes → depending on resistant between electrodes a measuring current flows
- measured resistance is converted into conductivity in mS/cm (typical unit for PeP) by: $\boldsymbol{\kappa = K/R}$
- with the cell constant $K = d\,/\,A$, influenced by distance (d) and area (A) of the electrodes

our **target: conductance $\boldsymbol{\kappa}$ of 100 – 140 mS/cm @ starting temperature (mostly 75 – 80 °C)**

Understanding Pep

material removal rate

material removal rate (MRR):

- mainly used to describe how fast PeP works (e.g. given in gramm per minute)
- influenced by a lot of factors:
  - part (material, geometry, size, surface (+area) and it‘s orientation (and or it‘s movement)
  - electrolyte (conductance, chemical reaktions, temperature, lifetime) and it‘s flow
  - process: voltage → current/amount of charge (time)

→ very specific value and difficult to compare if more than one condition is changed (and most are changing even during the process itself!)

sometimes better to find other specific rates:

- material removal per charge (gramm per ampere minute)
- material removal per area (gramm per cm^2)
- change of dimensions per time (µm/min) / per charge (µm/Amin) / …

Understanding Pep observations from the praxis

higher temperature: **lower MRR but higher material removel per charge**

→ PeP is slower but more efficient

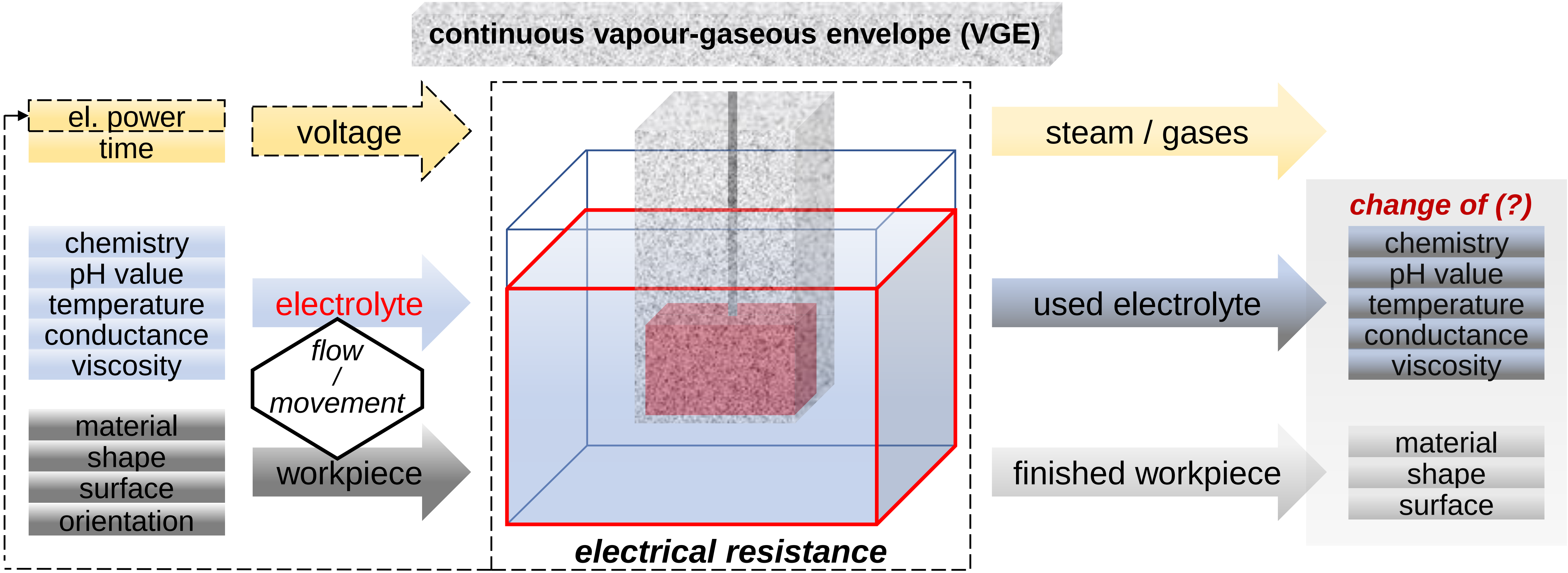
higher temperature: **higher removal at spikes (burrs, edges,…) than on flat areas**

UNDERSTANDING PEP

Part 2: Electrolyte Solutions

IMKF | Professur Additive Fertigung | Prof. Dr.-Ing. Henning Zeidler

Understanding Pep electrochemical cell



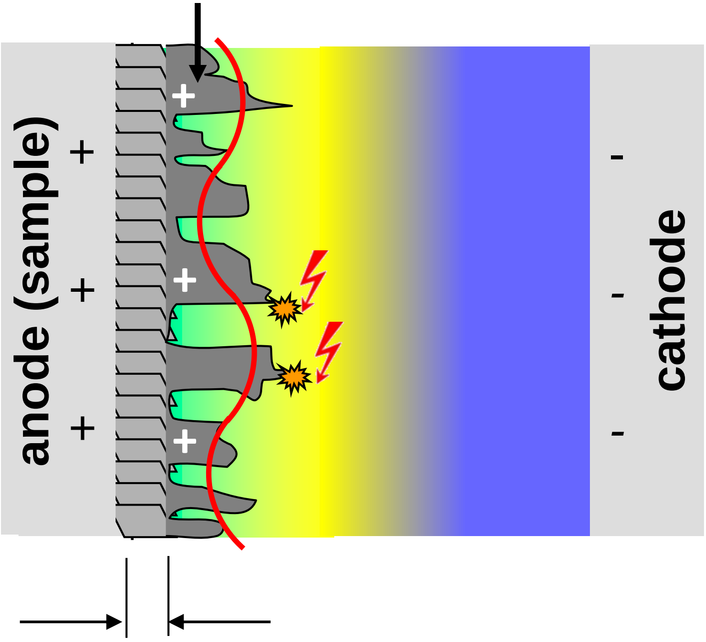
- chemistry of electrolyte solution is really important to achive material removal, surface smoothing and gloss

→ well working electrolyte composition has to be found for each single material/alloy

Understanding Pep

Material Removal Mechanisms

combination of electrochemical and physical processes



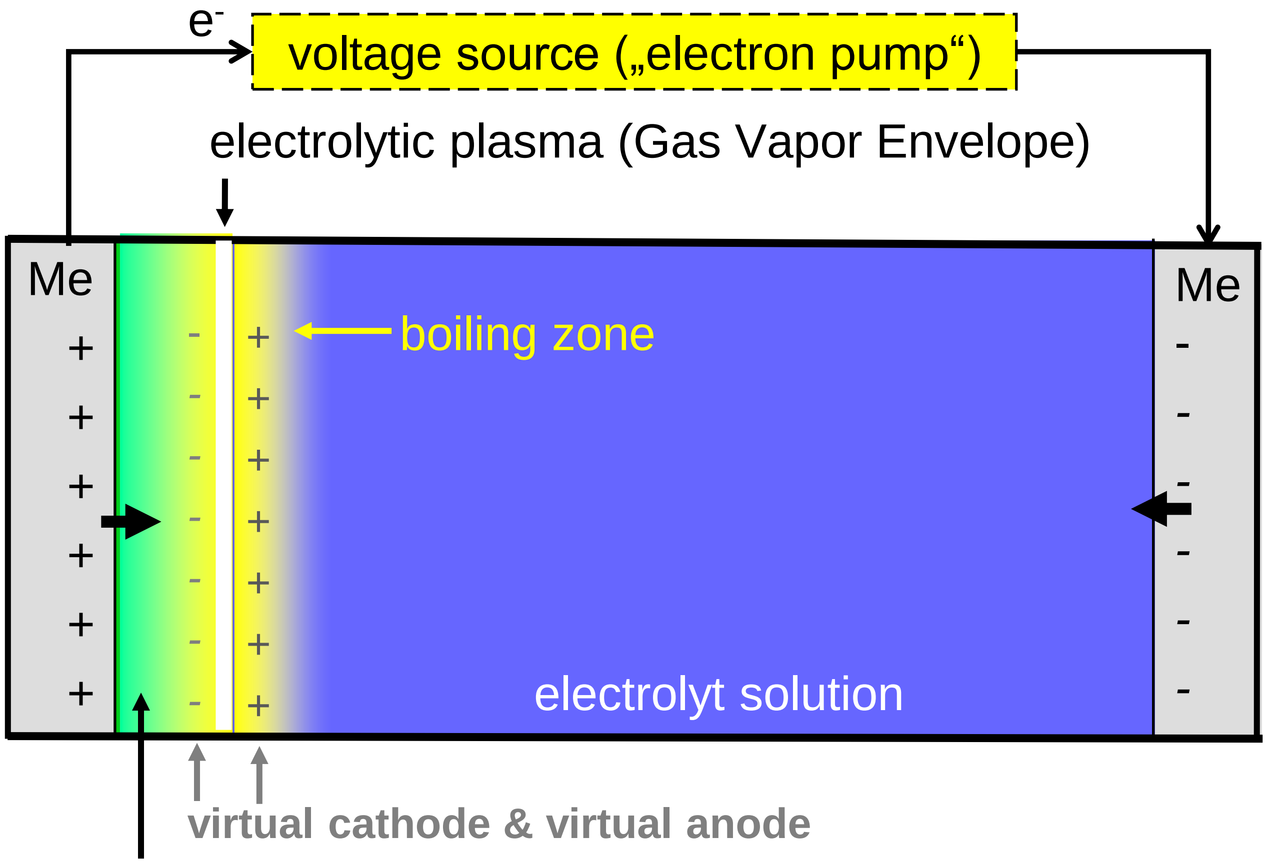
roughness
(micro bumps)

Processing boundary layer (energetically activated area)

mechanism	
electrolytic dissolution	applied voltage → electric field forms → metal ions dissolve from surface into electrolyte
plasma discharge	high voltage → plasma region with high-energy ions, electrons, and neutral atoms (highly reactive) → enables material removal from surface by preferentially attacking microscopic peaks
oxidation + chemical reactions	plasma state and presence of oxygen → forming of less stable oxides on surface → easier to remove
gas evolution	gas bubbles + rising → remove of abraded material residues

Understanding Pep

electrochemical cell/ reaction zones



anode
(sample)

anodic
metal dissolution
$Me \rightarrow Me^{x+} + x\, e^-$

x = 1: Na, Ag,…
x = 2: Cu, Fe, Ni,…
x = 3: Al,…
x = 4: Ti,…
x = 5: Mo, V,…

cathode

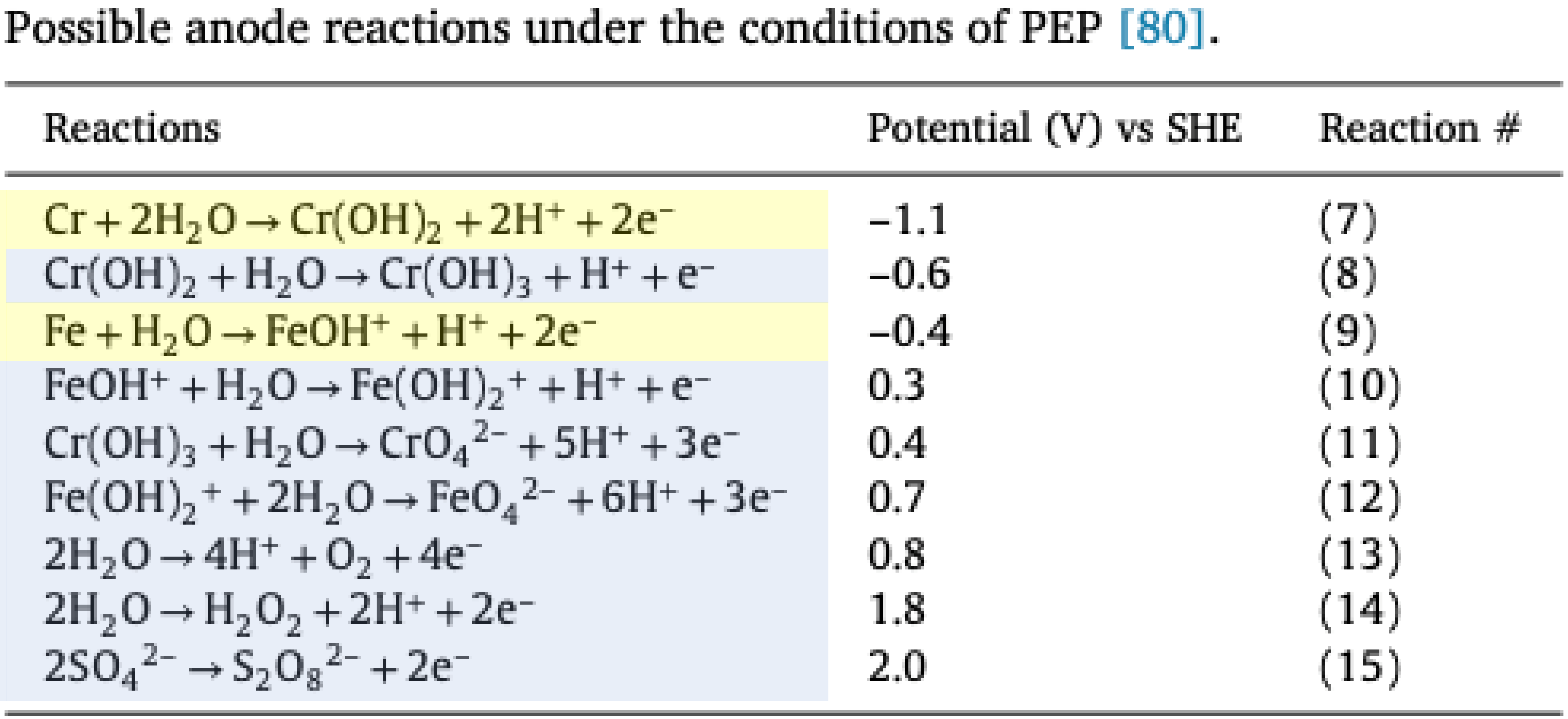
cathodic
reduction of water
$2\, H_2O + 2\, e^- \rightarrow H_2 + \underline{2\, OH^-}$

increases pH level

highly concentrated layer around the anode (*Helmholtz, Gouy-Chapman*)

boiling point 104 -108 °C (= max. temperature of anode, *discussed differently in literature*)

Understanding Pep reaction zones/electrochemical cell



Possible anode reactions under the conditions of PEP [80].

	Reactions	Potential (V) vs SHE	Reaction #
initial reactions at anode / cathode	$Cr + 2H_2O \rightarrow Cr(OH)_2 + 2H^+ + 2e^-$	−1.1	(7)
	$Cr(OH)_2 + H_2O \rightarrow Cr(OH)_3 + H^+ + e^-$	−0.6	(8)
	$Fe + H_2O \rightarrow FeOH^+ + H^+ + 2e^-$	−0.4	(9)
Further reactions with water and/or other ions in electrolyte	$FeOH^+ + H_2O \rightarrow Fe(OH)_2{}^+ + H^+ + e^-$	0.3	(10)
	$Cr(OH)_3 + H_2O \rightarrow CrO_4{}^{2-} + 5H^+ + 3e^-$	0.4	(11)
	$Fe(OH)_2{}^+ + 2H_2O \rightarrow FeO_4{}^{2-} + 6H^+ + 3e^-$	0.7	(12)
	$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$	0.8	(13)
	$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$	1.8	(14)
	$2SO_4{}^{2-} \rightarrow S_2O_8{}^{2-} + 2e^-$	2.0	(15)

formation of other ions or insoluble particles

Understanding Pep role of electrolyte

main task: absorption + retention of metal ions in solution

- water: → oxidation of Me
  → „produce“ VGE
- salts: → deliver ions as „charge carriers“ (mainly responsible for conductance)
- additives: eg. acids, bases, complexing agents
  → in some cases: remove oxid layer (anodic) to start the process
  → keep anodic reaction products in solution (e.g. metal ions or oxides)
  → prohibit formation of metal oxides on the metal surface

Electrolyte solution needs to deliver a suitable medium (environment, e.g. pH-level) to enable material removal, surface smoothing and increase of gloss!

Understanding Pep

examples

CrNi-steel @ acidic ammonium sulfate solution (sulfuric acid)

	Fe	Cr	Ni
Initial reaction (at anode)	Fe → Fe^+ + $2e^-$	Cr → Cr^{3+} + $3e^-$	Ni → Ni^{2+} + $2e^-$
Further reaction	$FeOH^+$ + H_2O → $Fe(OH)_2$ + e^- …	Cr^{3+} + SO_4^{2-} / NH_4^+→	Ni^{2+} + SO_4^{2-} →
Further reaction products	… → $(NH_4)Fe(SO_4)_2$ … → $Fe(OH)_3$	… → $Cr_2(SO_4)_3$ … → $(NH_4)Cr(SO_4)_2$	… → $NiSO_4$
Soluble (pH value)	**< ~ 3**	**< ~ 5 and > ~ 9**	**> ~ 10**
if not: precipitation of	insoluble red-brown depositions + mud	olive-green CrO(OH)-particles	light-green $Ni(OH)_2$-particles

- **pH < ~1.8: chemical etching (also without voltage) → rought and matte surface!**
- **content of Fe > ~72 % → firmly adhering black oxid-layer (FeO and/or Fe_3O_4)**

Understanding Pep examples

CrNi-steel @ sodium carbonate solution

	Fe	Cr	Ni
Initial reaction (at anode)	**nearly no reaction of Fe because oxidation of O_2 is energetically more favorable ($2\ Oh^- - 4e^- \rightarrow O_2 + H_2O$)**	**$Cr \rightarrow Cr^{3+} + 3e^-$**	$Ni \rightarrow Ni^{2+} + 2e^-$
Further reaction		$Cr^{3+} + OH^- \rightarrow Cr(OH)_3$	$Ni^{2+} + CO_3^{2-} \rightarrow NiCO_3$
Further reaction products		CrO_4^{2-} / $2\ Na^+ + CrO_4^{2-} \rightarrow Na_2CrO_4$	
Soluble (pH value)		> ~ 9	good
↳ **if not: precipitation of**		yellow sediment	light green

very very low material removal when polishing CrNi-steel in sodium carbonate solution *but* high gloss

Caution!: Fe-rich surface → lower oxidation resistance

Understanding Pep examples

CrNi-steel @ sodium carbonate solution

typical: orange glowing of ionised sodium

Understanding Pep examples

Copper @ acidic ammonium sulfate solution

→ development of copper sulfate layer ($CuSO_4$) on anode

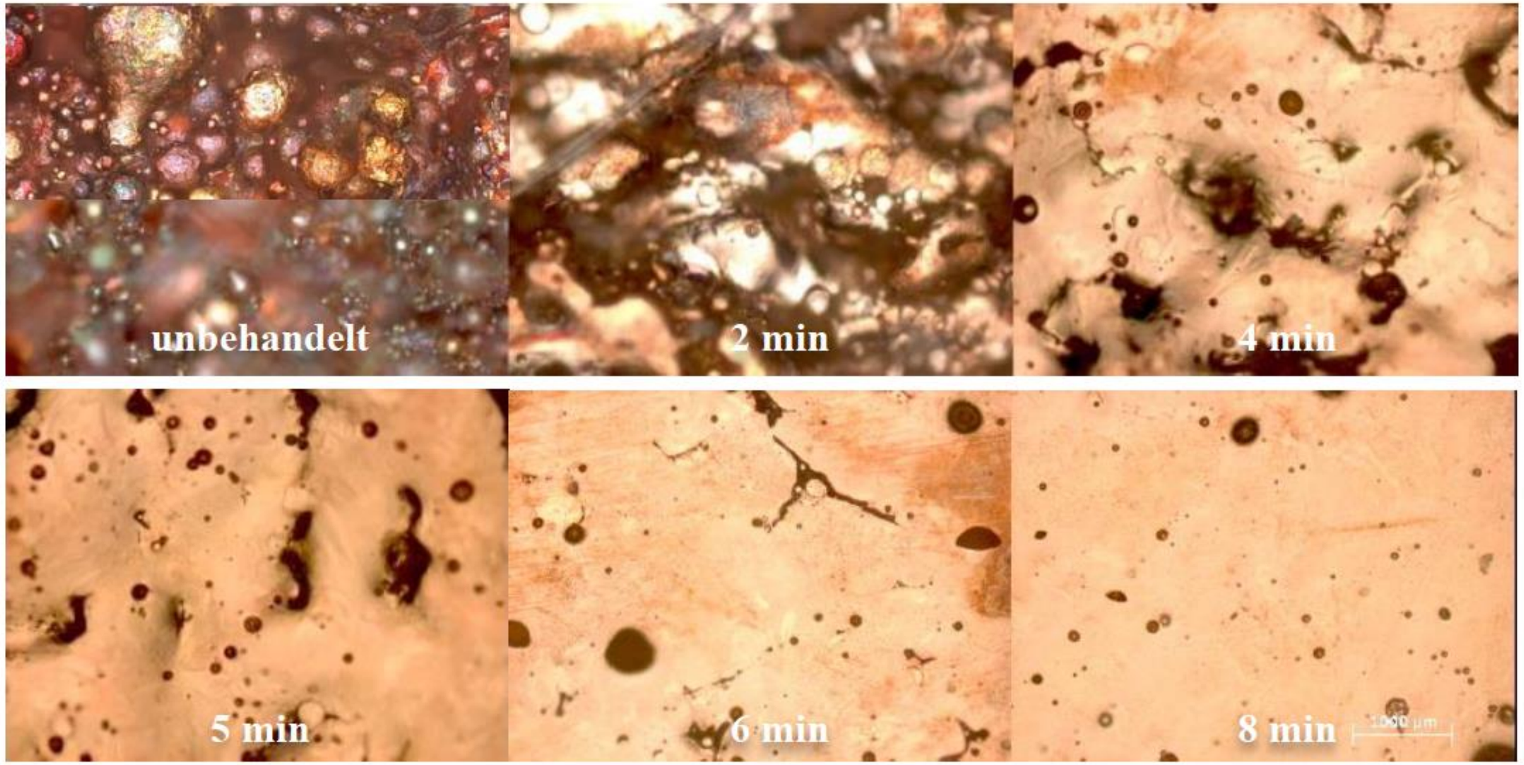
Copper @ ammoniacal ammonium sulfate solution

	Cu	
Initial reaction (at anode)	$Cu \rightarrow Cu^{2+} + 2e^-$	
Further reaction	$Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$	$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2$
Further reaction products	$\mathbf{[Cu(NH_3)_4]^{2+}} + 2OH^- \rightarrow Cu(OH)_2 + 4NH_3$	$CuO \cdot H_2O$
pH	**8.1 – 8.7**	**< ~ 9**
↳ **if not: precipitation of**	$CuSO_4$	unsoluble particles on anode

- ammonia (NH_3) acts as complexing agent and stable $[Cu(NH_3)_4]^{2+}$ is formed (Only between pH 8.1 – 8.7 and NH_3 is present! If not: light blue depositons and/or no gloss)
- high material removal rates + good surface smoothing + high gloss achievable

Understanding Pep

e.g.: Copper @ ammoniacal ammonium sulfate solution works well (see e.g. roughtness)



t [min]	Ra	Rq	Rz
0	11,15		73,85
2	3,30	3,60	13,71
3	1,96	2,51	8,45
4	1,40	1,83	7,35
5	1,01	1,31	5,71
6	0,56	0,88	4,65
7	0,49	0,71	2,89
8	0,44	0,71	3,48

Understanding Pep

difficult materials and options

material	difficulties	options
low-alloy steel	rust and chemical etching	no strong acids → use citric acid
carbon-rich steel	graphit-coating of cathode	?
valve metals/alloys (Al, Ti, Zr)	hard-to-destroy oxide layers, matte surfaces	fluoric acid (!)
Si-rich alloys	matte grey surfaces, no gloss	?

Understanding Pep post-treatment

- normaly its enough to rinse with water
- high gloss surfaces tend to show water spots → deionised water and fast drying with pressurised air
- corrosion sensitive metals/alloy: well washing + rinse with ethanol + drying (oven), store dry and in protective atmosphere,(i.e. oil-bags or in ethanol), don’t touch with bare hands
- rust from already corroded materials can be removed by PEP-treating them in citric acid-based electrolyte

Understanding Pep preparation of electrolyte solution

target: conductance κ of 100 – 140 mS/cm @ starting temperature (mostly 75 – 80 °C)

→ salts (e.g. ammonium sulfate, ammonium chloride, sodium carbonate) = basic for conductance

approximation: aqueous solutions → increase of conductivity = ~ 2 – 3 % per K (range between 25 – 100 °C)

conductance *κ* depends on concentration *c* and molar conductance *λ* of ions (X^{n+} and X^{n-}):

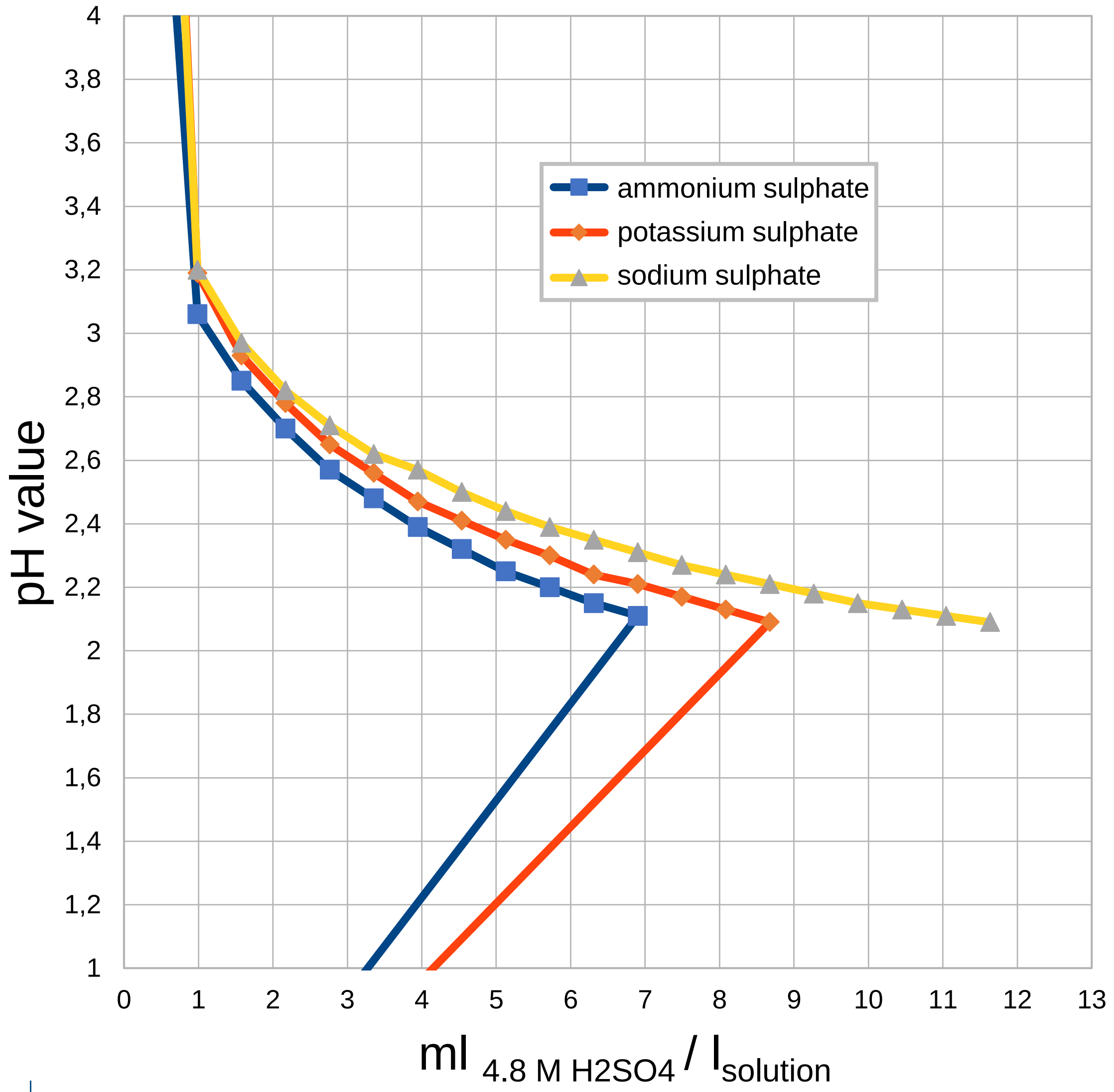
$$\kappa = c \cdot (\lambda_{Xn+} \cdot [X^{n+}] + \lambda_{Xn-} \cdot [X^{n-}])$$

target: suitable medium/environment (pH value) for required chemical reactions with anodic material

→ use of: acids, bases, complexing agents,…

other additives may influence conductance → take into account using the equation above!

Understanding Pep preparation of electrolyte solution

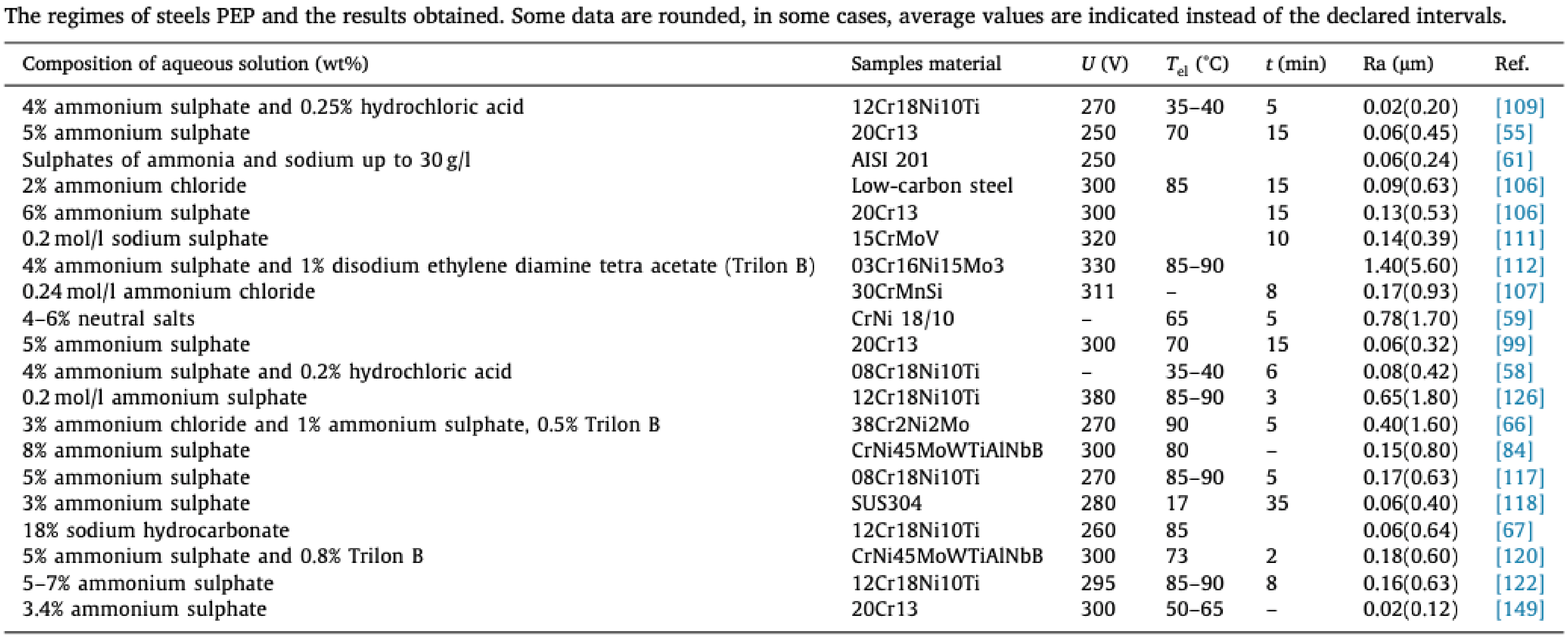


charts for resulting pH values **(measurements)** for different sulphatic solutions dependig on added 4.8 M sulphuric acid (ml/l)

4.8 M H_2SO_4 ≙ 37% sulphuric acid solution
→ reduced danger (e.g. “battery acid”)

→ **easy to read and practical and for daily work**

Understanding Pep preparation of electrolyte solution



The regimes of steels PEP and the results obtained. Some data are rounded, in some cases, average values are indicated instead of the declared intervals.

Composition of aqueous solution (wt%)	Samples material	U (V)	T_{el} (°C)	t (min)	Ra (µm)	Ref.
4% ammonium sulphate and 0.25% hydrochloric acid	12Cr18Ni10Ti	270	35–40	5	0.02(0.20)	[109]
5% ammonium sulphate	20Cr13	250	70	15	0.06(0.45)	[55]
Sulphates of ammonia and sodium up to 30 g/l	AISI 201	250			0.06(0.24)	[61]
2% ammonium chloride	Low-carbon steel	300	85	15	0.09(0.63)	[106]
6% ammonium sulphate	20Cr13	300		15	0.13(0.53)	[106]
0.2 mol/l sodium sulphate	15CrMoV	320		10	0.14(0.39)	[111]
4% ammonium sulphate and 1% disodium ethylene diamine tetra acetate (Trilon B)	03Cr16Ni15Mo3	330	85–90		1.40(5.60)	[112]
0.24 mol/l ammonium chloride	30CrMnSi	311	–	8	0.17(0.93)	[107]
4–6% neutral salts	CrNi 18/10	–	65	5	0.78(1.70)	[59]
5% ammonium sulphate	20Cr13	300	70	15	0.06(0.32)	[99]
4% ammonium sulphate and 0.2% hydrochloric acid	08Cr18Ni10Ti	–	35–40	6	0.08(0.42)	[58]
0.2 mol/l ammonium sulphate	12Cr18Ni10Ti	380	85–90	3	0.65(1.80)	[126]
3% ammonium chloride and 1% ammonium sulphate, 0.5% Trilon B	38Cr2Ni2Mo	270	90	5	0.40(1.60)	[66]
8% ammonium sulphate	CrNi45MoWTiAlNbB	300	80	–	0.15(0.80)	[84]
5% ammonium sulphate	08Cr18Ni10Ti	270	85–90	5	0.17(0.63)	[117]
3% ammonium sulphate	SUS304	280	17	35	0.06(0.40)	[118]
18% sodium hydrocarbonate	12Cr18Ni10Ti	260	85		0.06(0.64)	[67]
5% ammonium sulphate and 0.8% Trilon B	CrNi45MoWTiAlNbB	300	73	2	0.18(0.60)	[120]
5–7% ammonium sulphate	12Cr18Ni10Ti	295	85–90	8	0.16(0.63)	[122]
3.4% ammonium sulphate	20Cr13	300	50–65	–	0.02(0.12)	[149]

ammonium sulphate is often used because it (nearly) not take place in reaktions → no loss of it

Understanding Pep preparation of electrolyte solution

Calculation for amount of acid to be added to water / pH value

example of a acidic 0.33 M ammonium sulfate solution (sulphuric acid)

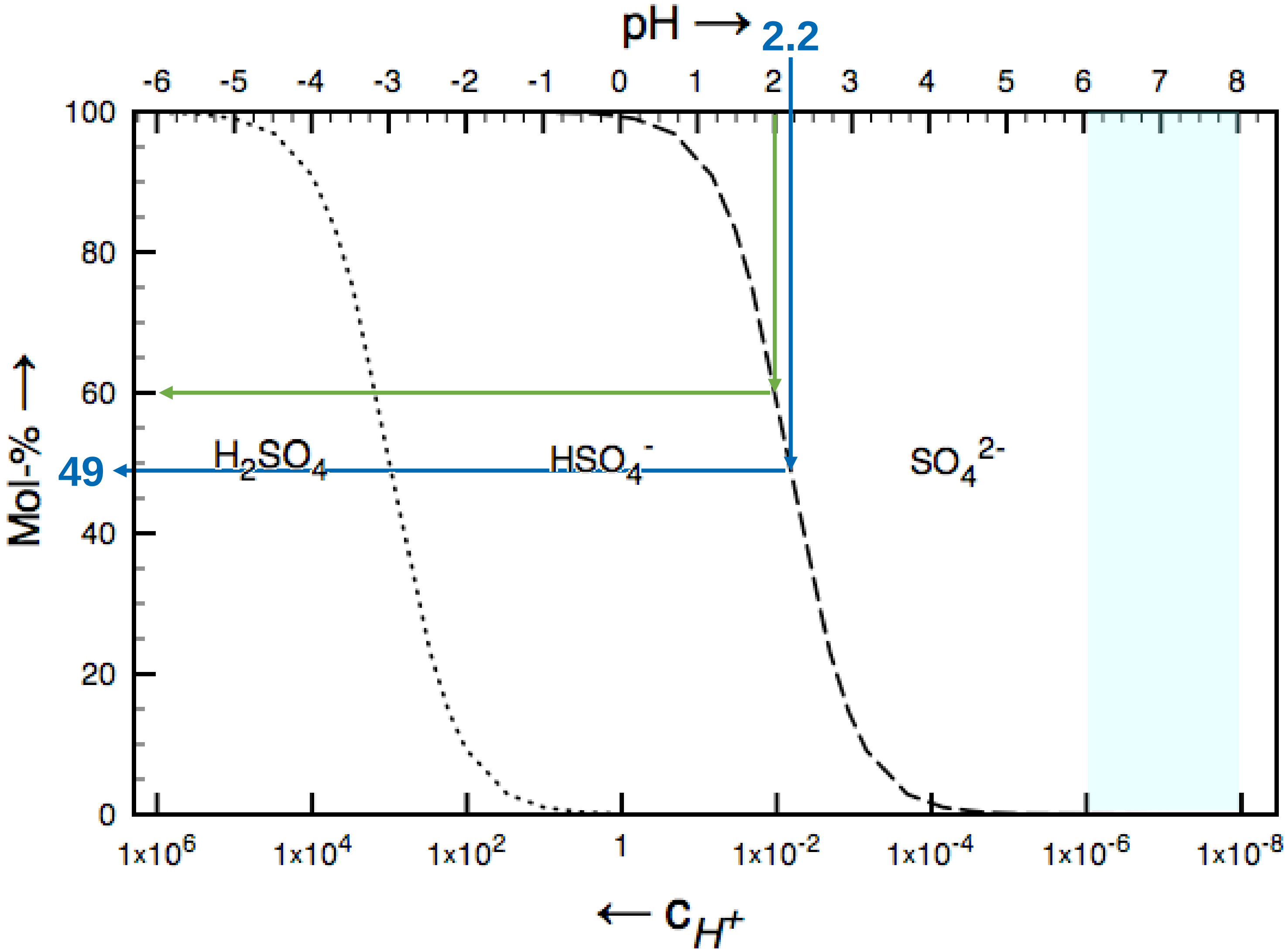
Henderson-Hasselbalch equation: $\mathrm{pH} = \mathrm{p}K_a + \log(c(\mathrm{A}^-) / c(\mathrm{HA}))$

pH…	acidity of the solution
pK_a…	**negative base-10 logarithm of the acid dissociation constant K_a** (acid dissociation constant at equilibrium state) *(1.99 for H_2SO_4 at equilibrium of hydrogen sulfat/sulfat)*
$c(\mathrm{A}^-)$…	concentration of the conjugate base / negative ion *(SO_4^{2-})*
$c(\mathrm{HA})$…	concentration of the associated acid *(HSO_4^-)*

→ **$c(\mathrm{HA}) = = c(\mathrm{A}^-) / 10^{\mathrm{pH - pKa}}$ *0.33 mol/l / $10^{2.2 - 1.92}$* = 0,1732 mol/l ??? → pH 2,71 ???**

→ **$c(\mathrm{HA}) = c(\mathrm{A}^-) / 10^{\mathrm{pH - pKa}}$ = *0.33 mol/l / $10^{2.2 - 1.99}$* = 0,2035 mol/l ??? → pH 2,2 ???**

Understanding Pep preparation of electrolyte solution



pH 2.2 →

49 Mol-% HSO_4^- equilibrium to

51 Mol-% SO_4^{2-}

pH 2.0 →

60 Mol-% HSO_4^- equilibrium to

40 Mol-% SO_4^{2-}

Understanding Pep preparation of electrolyte solution

Example: acidic 0.33 M ammonium sulfate solution (pH ~ 2.2)

- Calculation of incredient ammonium sulfate (44 g/l)
- Mixing (increased temperatur ~50 °C)
- pH (water + 0.33 M ammonium sulfate) ~ 6,3 – 6,4
- Calculation of incredient sulfuric acif (ca. 5.5 ml 4.8 M sulphuric acid / l)
- Slow dosing of sulfuric acid
- (Calculation of conductance)

Understanding Pep lifetime of electrolyte

lifetime:

- counted in the amount of charge as a value for how much metal is solved in electrolyte
- ends when required needs could not be achieved any more (gloss/roughtness or low MMR)
- mostly first gloss requirements could not be achieved but material removel is still given

refreshing:

- bring out metal elements by taking him the ability to solve them, e.g. change it‘s pH value → different metal compounds precipitate from the solution
- flocculating agent are helpfull to increase the agglomeration of small partikels
- sedimentation + decantig or filtering
- add required substances to bring it back to ist initial state (pH value)

environmental and user safety

Safety issue	Precaution
Hydrogen gas formation on the cathode	Gas exhaustion system
Hot electrolyte	Heat resistant work cloths
Chemical hazard	Safety glasses, gloves, lab coat, other equipment
Direct voltage	Electrical insulation
Halides are oxidised during PEP	Filtration system built-in in the gas exhaust system
Consumed electrolyte	Should be disposed according to the environmental safety requirements, i.e. cannot enter wastewater system

Understanding Pep environmental and user safety