ChemElectroChem

Supporting Information

Industrially Relevant Conditions in Lab-Scale Analysis for Alkaline Water Electrolysis

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Calculation of Ag/AgCl reference electrode potential

To the best of our knowledge, the equilibrium potential for an Ag/AgCl containing 3.5 M KCl at 80 °C is only reported for a pH value of 0 in the literature/manufacturer's brochures and accounts for 155.6 mV *vs*. RHE.[54] Therefore, the theoretical potential must be corrected for the pH value using the Nernst equation. The pH of 30 wt.% KOH is reported to be approximately 13.7 at 80 °C and 14 for 1 M KOH at RT.[55] According to eq. 1.1-1.3, this results in a theoretical RE potential of 1.114 V for 30 wt.% at 80 °C. and 1.029 V for 1 M KOH at RT.

$$E_{\mathrm{Ag/AgCl}}\,(\mathrm{T},\mathrm{pH}\,) = E_{\mathrm{Ag/AgCl}}\,(T,0) + 2{,}3026 \cdot \left(\frac{\mathrm{R}T}{\mathrm{F}}\right) \cdot pH \tag{1.1}$$

$$E_{\mathrm{Ag/AgCl}}\,(80°\mathrm{C},\mathrm{pH}\ 13.7) = (255\ +\ 70\ \cdot pH)\ \mathrm{mV}\ vs.\mathrm{RHE} = 1{,}114\ \mathrm{mV}\ vs.\mathrm{RHE} \tag{1.2}$$

$$E_{\mathrm{Ag/AgCl}}\,(25°\mathrm{C},\mathrm{pH}\ 14) = (203.7\ +\ 59\ \cdot pH)\ \mathrm{mV}\ vs.\mathrm{RHE} = 1{,}029\ \mathrm{mV}\ vs.\mathrm{RHE} \tag{1.3}$$

Tabular presentation of the presented electrochemical protocol

Step	Conditioning	
1	OCP	2 h
2	CV	t.b.a.

Step	Activity Measurement	
3	CS	x – 10 mA cm^{-2} ; 10 mA cm^{-2} s^{-1}
4	CP	10 mA cm^{-2} ; 3 min
5	GEIS	10 mA cm^{-2}; (200 kHz – 1 kHz); i_A= 1 mA cm^{-2}
6	CS	10 – 100 mA cm^{-2} ; 10 mA cm^{-2} s^{-1}
7	CP	100 mA cm^{-2} ; 3 min
8	GEIS	100 mA cm^{-2}; (200 kHz – 1 kHz); i_A= 10 mA cm^{-2}
9	CS	100 – 500 mA cm^{-2} ; 10 mA cm^{-2} s^{-1}
10	CP	500 mA cm^{-2} ; 3 min
11	GEIS	500 mA cm^{-2}; (200 kHz – 1 kHz); i_A= 50 mA cm^{-2}
12	CS	500 – 1000 mA cm^{-2} ; 10 mA cm^{-2} s^{-1}
13	CP	1000 mA cm^{-2} ; 3 min
14	GEIS	1000 mA cm^{-2}; (200 kHz – 1 kHz); i_A= 100 mA cm^{-2}

Step	Stressor				Step
	Constant Load		Alternating Load (AST)		
15a	CP	1000 mA cm^{-2} ; 2 h	CP	1000 mA cm^{-2} ; 1 min	15b
16b	Loop	Return to step 3 for > 25x	CS	1000 - 750 mA cm^{-2} ; 250 mA cm^{-2} s^{-1}	16b
			CP	750 mA cm^{-2} ; 1 min	17b
			CS	750 - 1000 mA cm^{-2} ; 250 mA cm^{-2} s^{-1}	18b
			CP	1000 mA cm^{-2} ; 1 min	19b
			CS	1000 - 500 mA cm^{-2} ; 250 mA cm^{-2} s^{-1}	20b
			CP	500 mA cm^{-2} ; 1 min	21b
			CS	500 - 1000 mA cm^{-2} ; 250 mA cm^{-2} s^{-1}	22b
			CP	1000 mA cm^{-2} ; 1 min	23b
			CS	1000 - 250 mA cm^{-2} ; 250 mA cm^{-2} s^{-1}	24b
			CP	250 mA cm^{-2} ; 1 min	25b
			CS	250 - 1000 mA cm^{-2} ; 250 mA cm^{-2} s^{-1}	26b
			CP	1000 mA cm^{-2} ; 1 min	27b
			CS	1000 - 0 mA cm^{-2} ; 250 mA cm^{-2} s^{-1}	28b
			CP	0 mA cm^{-2} ; 1 min	29b
			CS	0 - 1000 mA cm^{-2} ; 250 mA cm^{-2} s^{-1}	30b
			CP	1000 mA cm^{-2} ; 1 min	31b
			CS	1000 - 250 mA cm^{-2} ; 250 mA cm^{-2} s^{-1}	32b
			CP	250 mA cm^{-2} ; 1 min	33b
			CS	250 - 1000 mA cm^{-2} ; 250 mA cm^{-2} s^{-1}	34b
			CP	1000 mA cm^{-2} ; 1 min	35b
			CS	1000 - 500 mA cm^{-2} ; 250 mA cm^{-2} s^{-1}	36b
			CP	500 mA cm^{-2} ; 1 min	37b
			CS	500 - 1000 mA cm^{-2} ; 250 mA cm^{-2} s^{-1}	38b
			CP	1000 mA cm^{-2} ; 1 min	39b
			CS	1000 - 750 mA cm^{-2} ; 250 mA cm^{-2} s^{-1}	40b
			CP	750 mA cm^{-2} ; 1 min	41b
			CS	750 - 1000 mA cm^{-2} ; 250 mA cm^{-2} s^{-1}	42b
			Loop	Return to Step 15 for 7x (~2h)	43b
			Loop	Return to step 3 for > 25x	44b

Table S1. Tabular presentation of the presented electrochemical protocol, divided into conditioning, activity measurement and the stressor. As stressors, either a constant or alternating load can be carried out. (OCP = open circuit potential; CV = cyclic voltammetry; CS = current scan; GEIS = galvanostatic electrochemical impedance spectroscopy)

Technical drawing of the beaker cell lid

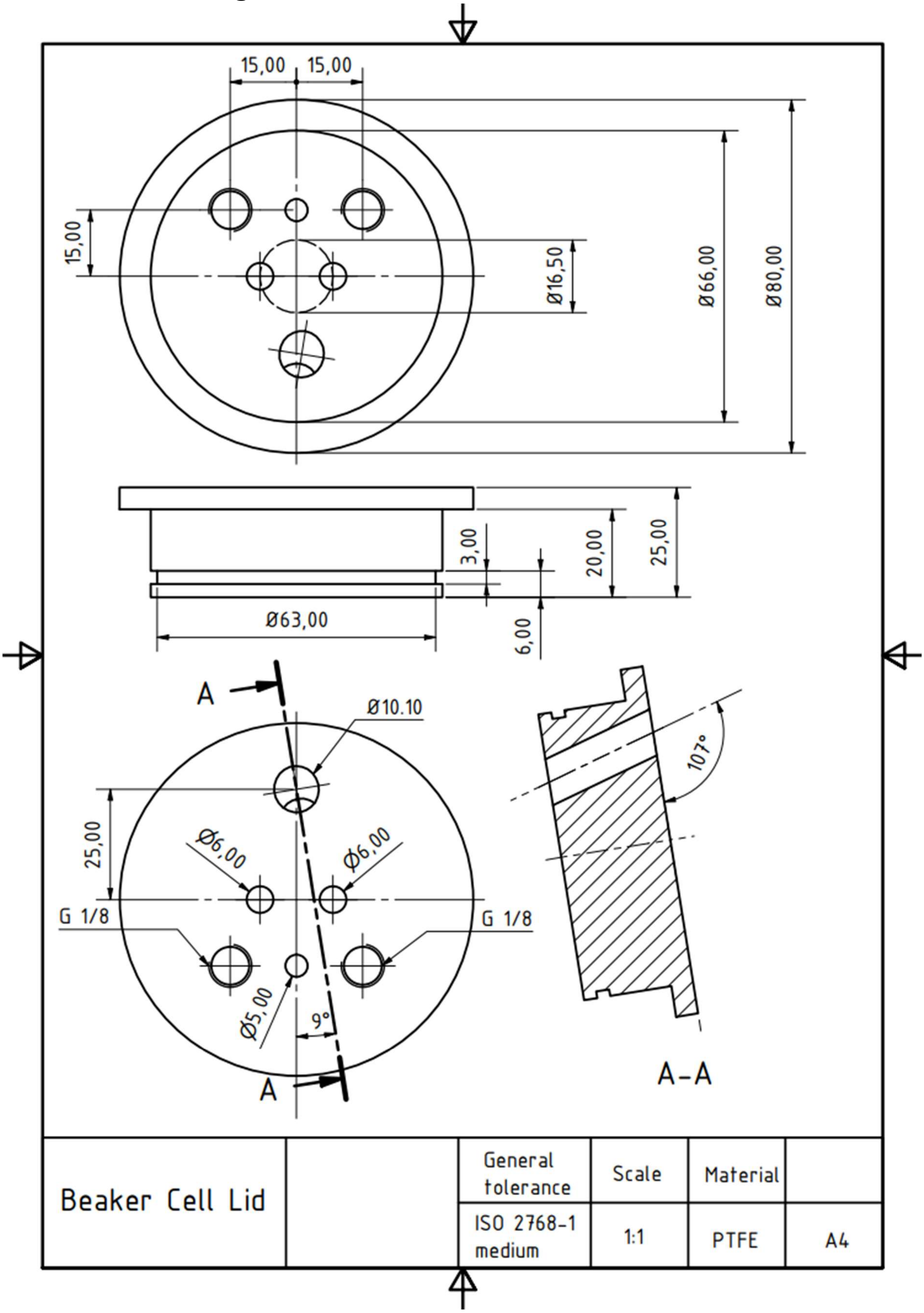

Figure S1. Technical drawing of the PTFE lid for the beaker cell

Laboratory picture of the beaker cell setup

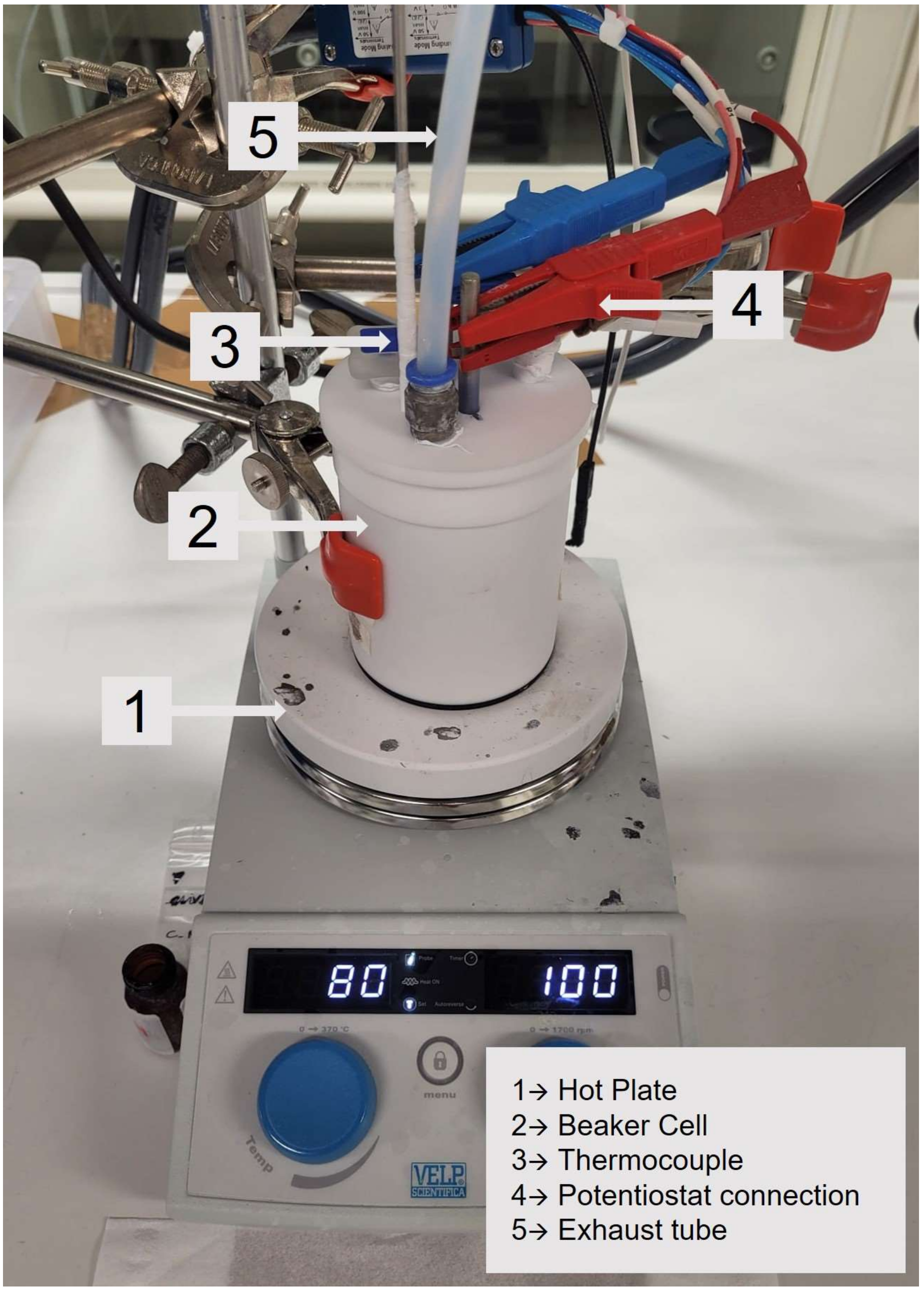

Figure S2. Picture of the complete beaker cell setup in the laboratory.

Stability of leakless Ag/AgCl under mild conditions

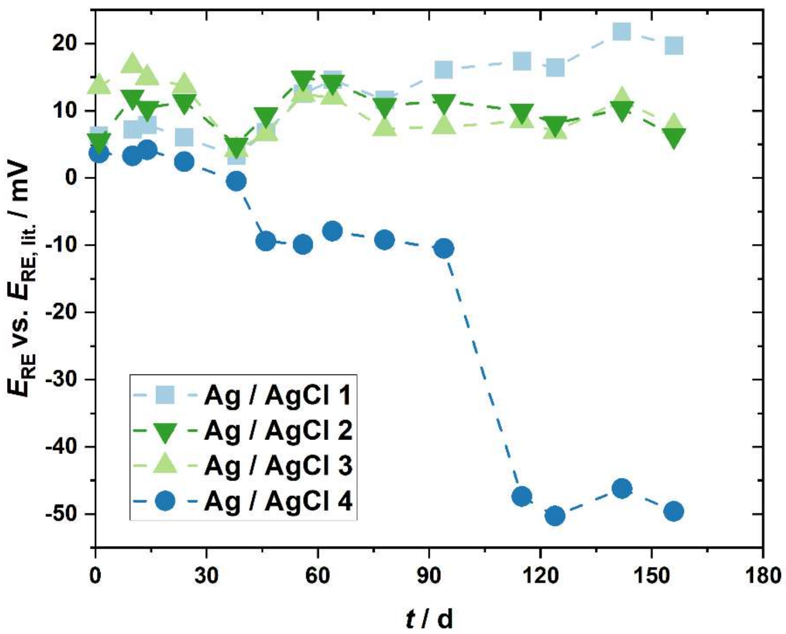

Figure S3. Detailed potential profile of 4 leakless Ag/AgCl REs (Innovative Instruments Inc.) for a total of 160 days in mV against reported literature value of 1,029 mV *vs.* RHE. All potentials were obtained by OCP measurements against a master Ag/AgCl. REs were exposed to 1 M KOH at RT during day-to-day lab work, the master-Ag/AgCl was frequently measured against a true RHE.

Technical drawing of Ni tuck-in holder

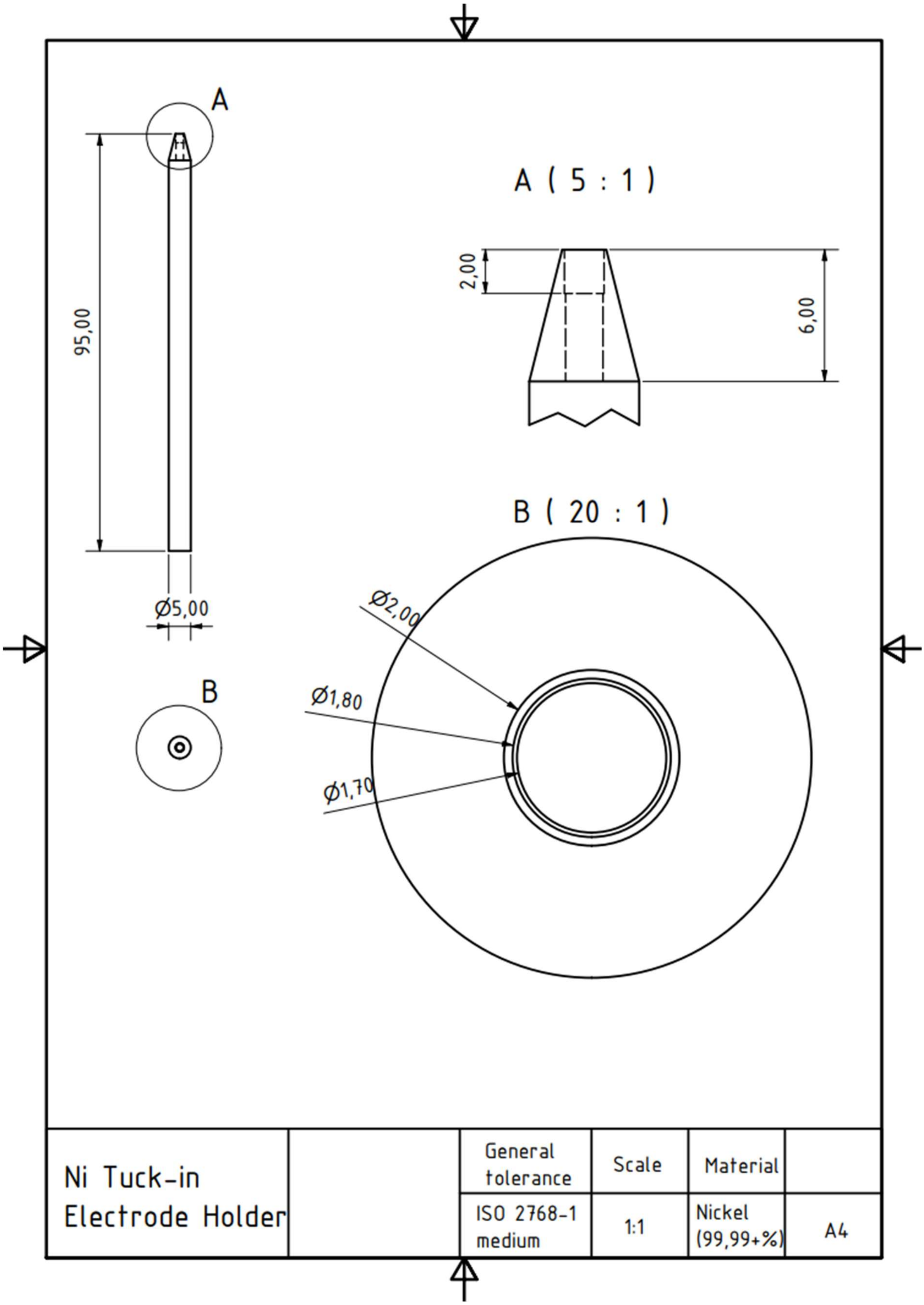

Figure S4. Technical drawing of the Ni tuck-in holder.

Electrode holder manufacturing process

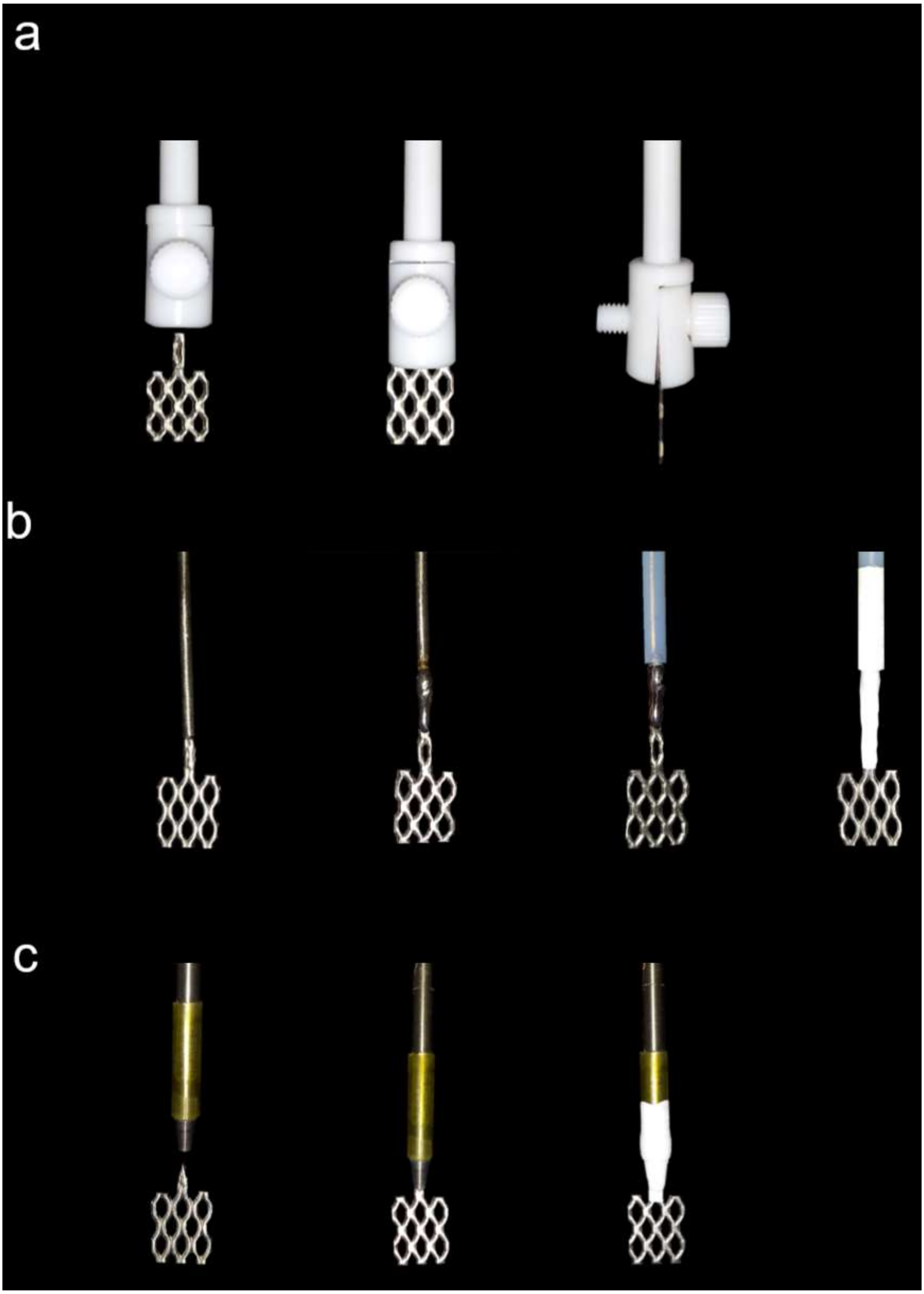

Figure S5. Electrode holder production sequence for: Commercial electrode holder (a), electrode soldered/welded to a Ni rod and PTFE sealed (b), electrode build in an in-house designed Ni tuck-in holder and sealed with PTFE (c).

Long-term uncompensated resistance for electrode holders

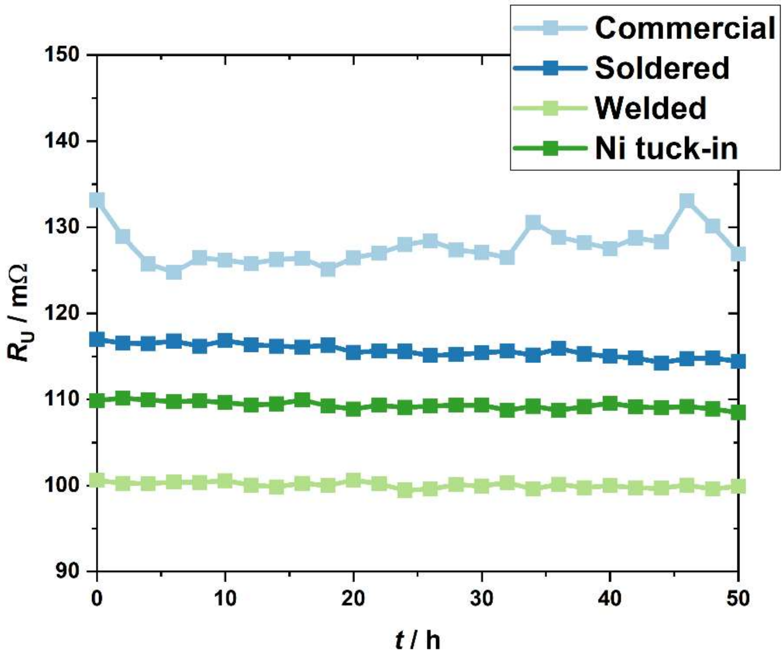

Figure S6: Uncompensated resistance (R_U) measured via EIS at 10 mA cm^{-2} over a time period of 50 hours shown for the commercial, the soldered, the welded and the Ni tuck-in electrode holder.