Supporting Information

Investigation of CO_2 electrolysis on tin foil by electrochemical impedance spectroscopy

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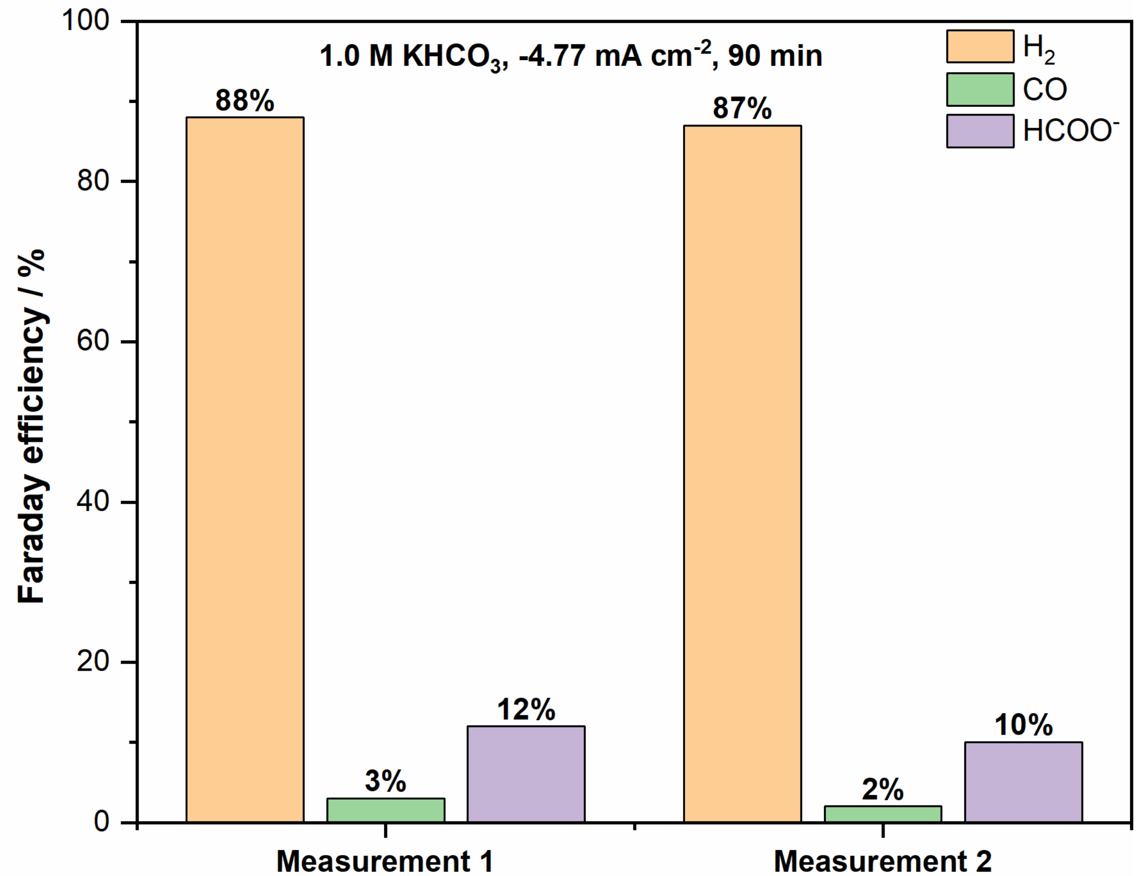

Figure S1 Faraday efficiency determination of H_2, CO and $HCOO^-$ after galvanostatic operation at - 4.77 mA cm^{-2} in CO_2 saturated 1.0M $KHCO_3$ aqueous solution showing reproducible results and by that validating the test set-up. During EIS measurements shown in the primary paper further liquid phase $HCOO^-$ determination was skipped due to the lack of possibility to quantify $HCOO^-$ online. H_2 and CO were quantified online via µ-GC and used to calculate the faraday efficiency for formate via the mass balance closing condition.

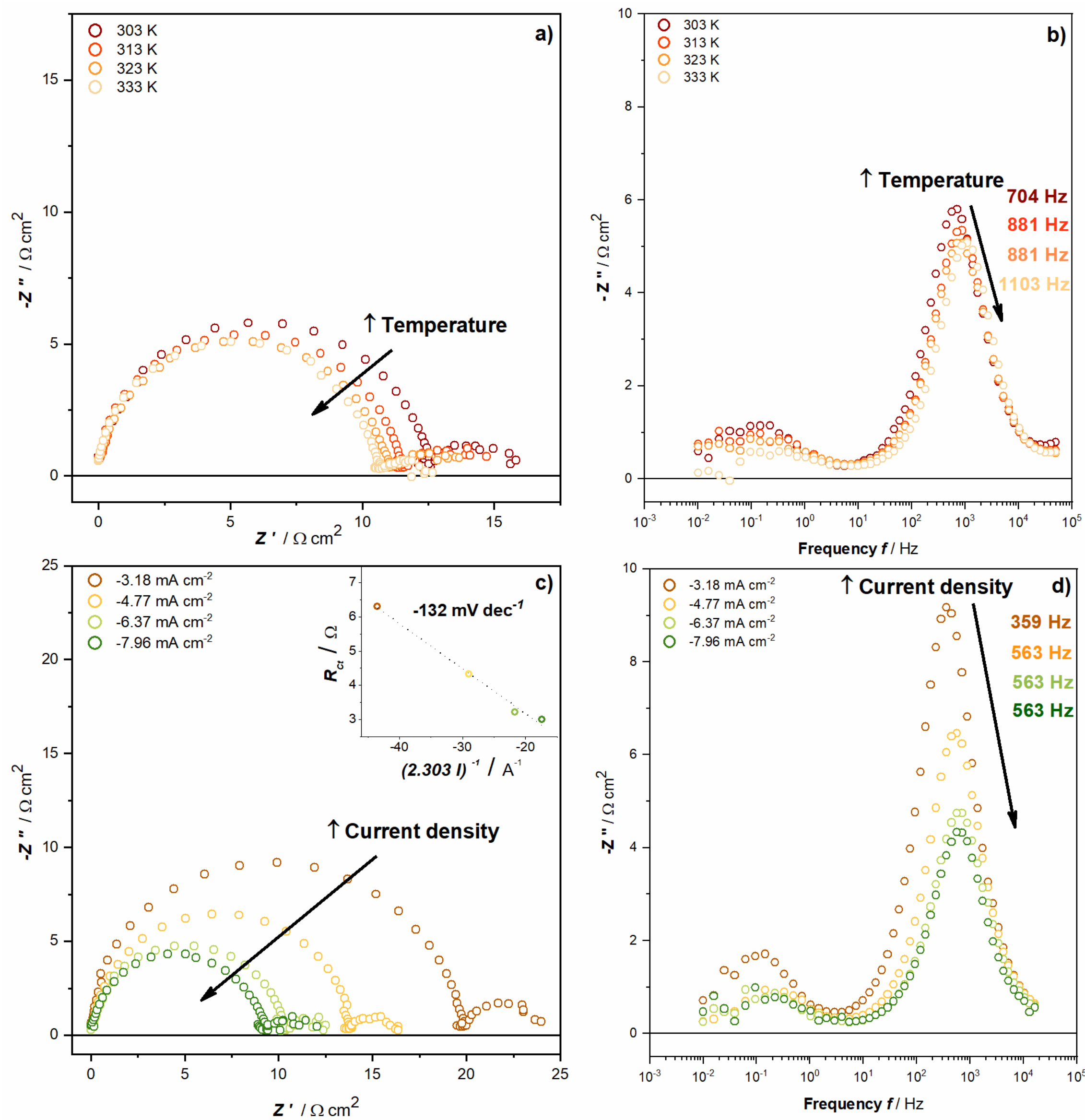

Figure S2 –Nyquist plots for tin foil (ohmic resistance subtracted) of **a)** temperature and **c)** current density parameter series to identify thermal and current activated processes in 1.0 M $KHCO_3$ solution and their corresponding imaginary part vs. frequency plots **b), d)**. Inset **c)** Tafel slope determination via R_{Ct} vs. I^{-1} plot.

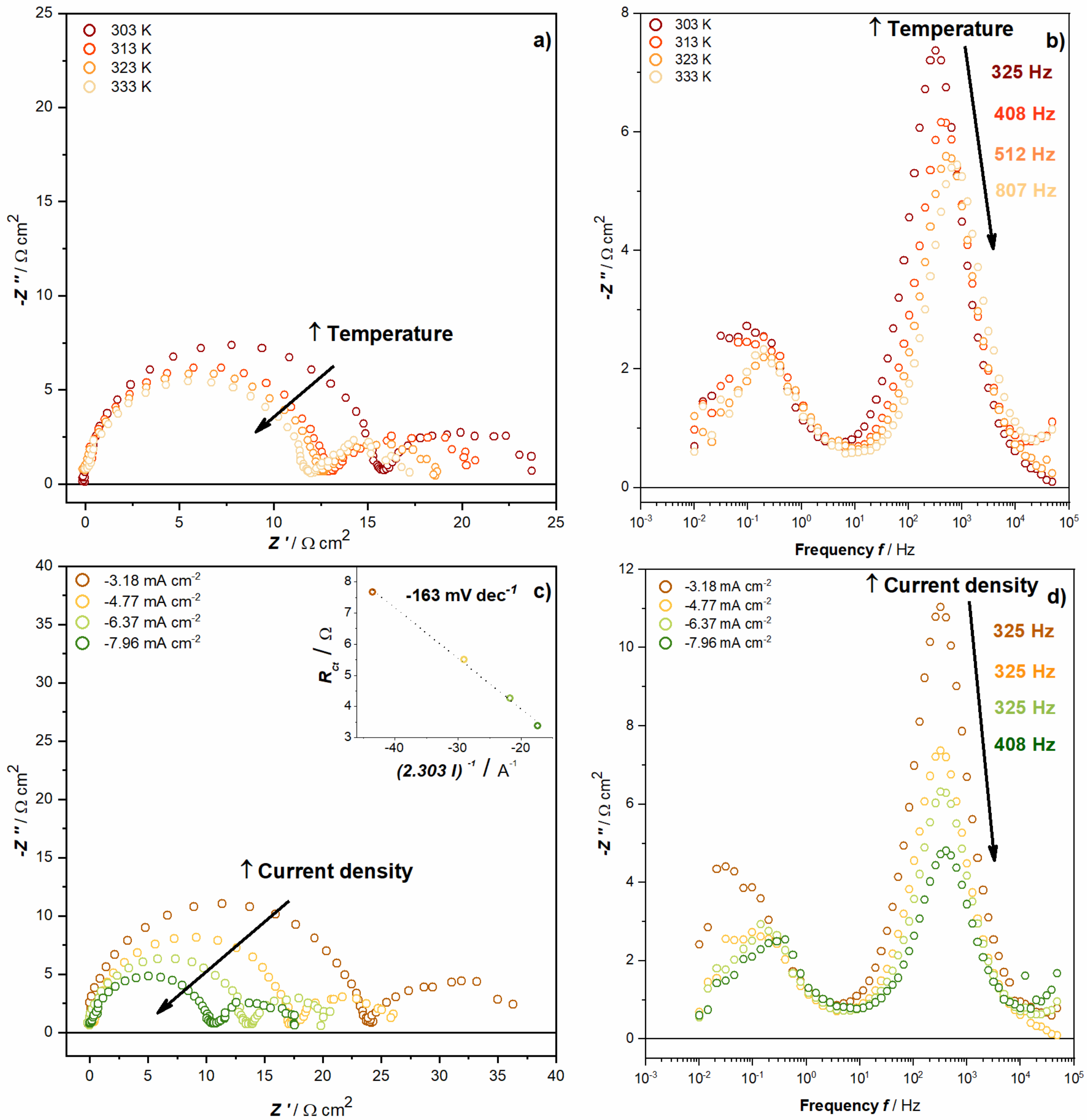

Figure S3 –Nyquist plots for tin foil (ohmic resistance subtracted) of **a)** temperature and **c)** current density parameter series to identify thermal and current activated processes in 0.1 M $KHCO_3$ solution and their corresponding imaginary part vs. frequency plots **b), d)**. Inset **c)** Tafel slope determination via R_{Ct} vs. I^{-1} plot.

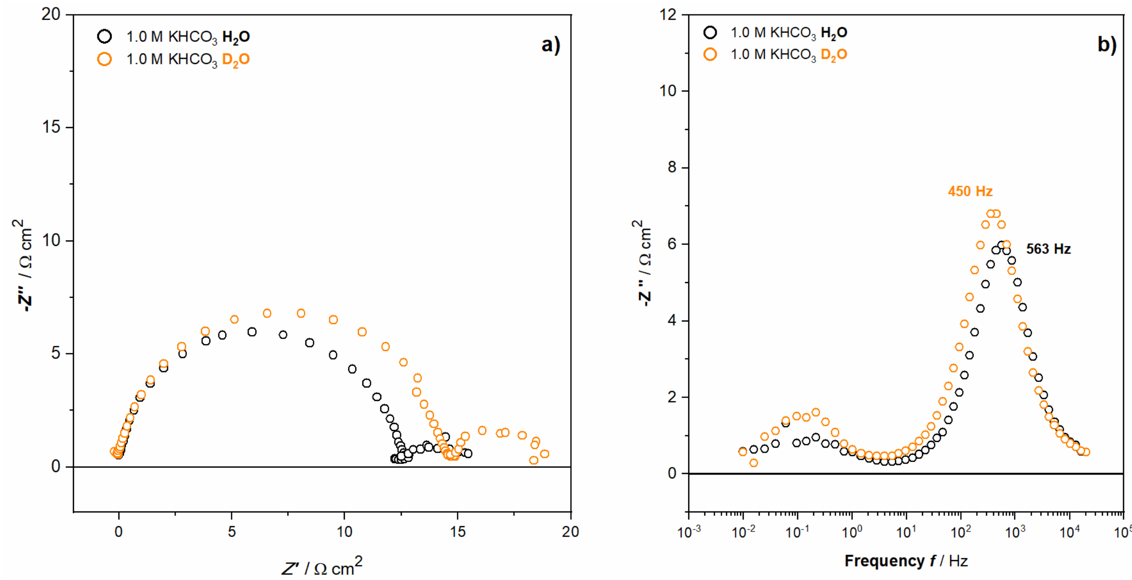

Figure S4 Impedance spectra **a)** and **b)** imaginary part vs. frequency plot for tin foil obtained in CO_2 saturated 1.0 M $KHCO_3$ solution comparing H_2O and D_2O as solvent. Galvanostatic operation at – 4.77 mA cm^{-2} with an amplitude of 5mA, ohmic resistance subtracted.

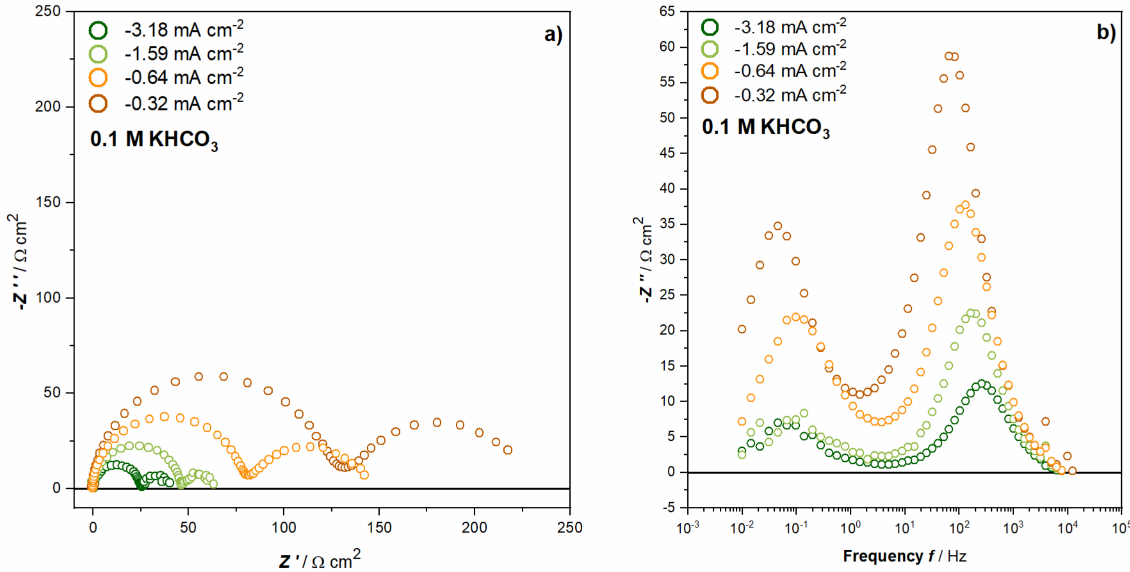

Figure S5 Impedance spectra **a)** and **b)** imaginary part vs. frequency plot for tin foil obtained in CO_2 saturated 0.1 M $KHCO_3$ solution for low current densities. Galvanostatic operation at desired current densities with an amplitude of 5mA, ohmic resistance subtracted.

In contrast to S3 c) and d) the low frequency process clearly depends on the applied current for extremely low current levels. However, further investigation would go beyond the scope of this contribution since at these low current densities, respectively potentials, the EIS response is almost completely determined by HER and the product analysis unreliable (due to low current densities resulting in low conversion rates). Therefore, the faraday efficiency for CO_2RR is almost negligible, thus, with low relevance to the target of this investigation.

Table S1 Resistance and Capacitor values inserted into Thales® EQCM modelling tool. Time constant τ, R_{mixed} and C_{mixed} calculated via Equation S1-S3.

Ratio time constants	R_{HER} / Ω	C_{HER} / F	τ_{HER} / s	R_{CO2RR} / Ω	C_{CO2RR} / F	τ_{CO2RR} / s	R_{mixed} / Ω	C_{mixed} / F	τ_{mixed} / s
$\tau_1 = \tau_2$	1	0.01	0.01	1	0.01	0.01	0.5	0.02	0.01
$5\ \tau_1 = \tau_2$	1	0.01	0.01	2.5	0.02	0.05	0.714	0.03	0.021
$100\ \tau_1 = \tau_2$	1	0.01	0.01	10	0.1	1	0.909	0.11	0.100
$1000\ \tau_1 = \tau_2$	1	0.01	0.01	20	0.5	10	0.952	0.510	0.486

$$\tau = R \bullet C \tag{S1}$$

$$\frac{1}{R_{mixed}} = \frac{1}{R_{HER}} + \frac{1}{R_{CO2RR}} \tag{S2}$$

$$C_{mixed} = C_{HER} + C_{CO2RR} \tag{S3}$$