## **Supporting Information**

## Revealing mechanistic processes in gas-diffusion electrodes during CO2 reduction via impedance spectroscopy

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**Figure S1** Schematic drawing of electrolysis cell with 3 electrode configuration. Reference electrode: Reversible hydrogen electrode (RHE); Counter electrode: Platinum; Working electrode: in-house manufactured carbon supported tin based gasdiffusion electrode (GDE). The electrolysis cell including electrolyte (1.0 M KOH\*aq) vessel were put into a water bath for tempering.

Estimation CO<sub>2</sub> flow rate error

Since the inlet flow rate of CO<sub>2</sub> was used to calculate the FEs for the gas phase products a slight error occurs due to the reaction of CO<sub>2</sub> with OH<sup>-</sup> present in the electrolyte and OH<sup>-</sup> ions produced by electrochemical reactions. These phenomena reduce the real CO<sub>2</sub> outlet flow rate so that the FEs calculated with the species concentrations (measured via µ-GC) and the CO<sub>2</sub> inlet flow rate are higher than the ones calculated with the outlet flow rate. Seger et al. recently showed that under open circuit voltage (no current load) the CO<sub>2</sub> inlet flow rate is reduced in the outlet from 45 mL min<sup>-1</sup> to approximately 43.5 mL min<sup>-1</sup> when using a Cu coated GDE as cathode in 1.0 M KOH. The geometrical surface area was 2 cm<sup>2,1</sup> In our system operating in 1.0 M KOH the CO<sub>2</sub> inlet flow was 50 mL min<sup>-1</sup> and the geometrical surface area of the GDE 1 cm<sup>2</sup>. Estimated conservatively using the data from Seger et al., the error for the CO<sub>2</sub> flow rate due to conversion with OH<sup>-</sup> of the electrolyte is about 1.5 mL min<sup>-1</sup>. Additionally, the error induced by the conversion of CO<sub>2</sub> with OH<sup>-</sup> produced by electrochemical reactions can be estimated via Faradays law and the ideal-gas law assuming: I = 0.05 A (standard current during parameter series, except current density series), z = 2, F = 96485 A s mol<sup>-1</sup>, T = 30 °C, p = 101300 Pa and R = 8.31451 J K<sup>-1</sup>

mol<sup>-1</sup>. After calculation the error can be estimated to be around 0.4 mL min<sup>-1</sup>. Adding up both errors described above, the total error when using the  $CO_2$  inlet instead of outlet flow rate is ~ 2.0 mL min<sup>-1</sup> which is 4% referenced to the inlet flow rate of 50 mL min<sup>-1</sup>. In relation to the gas phase products FEs, which are around 5% up to 15%, the absolute errors of the FEs are in the range of 0.2% and 0.6% which are insignificant.

The outcome of the physical characterization measurements is summarized in Figure S2. Figure S2 a) displays a SEM image of the GDE recorded with an acceleration voltage of 2.0 kV and a magnification of 20k. The heterogeneity of the microstructure becomes evident revealing a porous structure of the GDE which is essential for the functionality of the GDE. Taking the results of the mercury intrusion porosimetry (MIP) into account (cf. Figure S2 c)) the porosity of the electrode is about 81% and a bimodal pore size distribution is observed which is characteristic of carbon black-based GDEs. The pore diameters are ~ 3.8 µm and 90 nm. This bimodal pore system is of utmost importance for a well-performing GDE since both of the pore types fulfill a specific task during the reaction. The bigger pores with diameter above 100 µm, in literature often denoted the secondary pore system and ascribed to the voids between the carbon black applomerates, ensure a fast transport of gaseous CO2 inside the electrode whereas the agglomerates with pores < 100 µm are filled with the electrolyte due to capillary forces.<sup>2</sup> For a chemical reaction to happen,  $CO_2$  must be transported to the active sites:  $CO_2$ dissolves at the gas / liquid interface inside the GDE whereas this interface significantly

exceeds the geometrical surface area. Subsequently,  $CO_2$  diffuses through the liquid phase to the active sites and is converted to carbonaceous products. The outstanding advantage of GDEs is that the diffusion length of  $CO_2$  from the gas / liquid interface to the active sites is dramatically decreased compared to bulk diffusion in set-ups using plane cathodes. Beside the per geometrical surface area increased number of active sites, this the reason why GDEs achieve high conversion rates for  $CO_2RR$ . <sup>2-4</sup>

The SEM picture in **Figure S2 b)** obtained with an angle-selective back scattered electron detector shows the material contrast between the carbon network and the catalyst particles (brighter) pointing out the uniform catalyst dispersion inside the GDE. As shown previously, the particles have a diameter of around 10 nm – 40 nm while additional TEM measurements revealed that the observable catalyst particles are agglomerates consisting of crystallites with a diameter below 3 nm.<sup>4</sup>

The bonding condition at the surface of the GDE was investigated *via* XPS (cf. **Figure S2 d)**). The inset of the diagram shows the region of interest where the catalyst material, Sn, is specified. At about 495.4 eV and 486.9 eV one can see the peaks for the Sn3d<sub>3/2</sub> & Sn3d<sub>5/2</sub> orbital which is attributed to Sn(+II, +IV)O<sub>x</sub> ruling out the existence

of metallic Sn (Sn3d<sub>3/2</sub> = 492.8 eV, Sn3d<sub>5/2</sub> = 484.5 eV) on the catalyst surface inside the GDE. <sup>5, 6</sup> Unfortunately, we were not able to distinguish between SnO and SnO<sub>2</sub> with the XPS data at hand which can be traced back to the small differences in binding energies (SnO: Sn3d<sub>3/2</sub> = 494.7 eV, Sn3d<sub>5/2</sub> = 486.3 eV ; SnO<sub>2</sub>: Sn3d<sub>3/2</sub> = 495.4 eV, Sn3d<sub>5/2</sub> = 486.9 eV).<sup>5, 6</sup>

Despite not being able to distinguish between the oxide species on the surface, it is important to generally conclude that tin oxide rather than metallic tin is present on the surface. It was shown that a meta stable tin oxide layer is present during electrochemical conversion of CO<sub>2</sub> under reducing potentials.<sup>7</sup>

Additional XRD measurements were conducted for the tin catalyst which was, in contrast to the above described procedure, directly precipitated and not on carbon support. Thermal treatment of the tin catalayst was performed as described in the experimental section. The diffractometer of the material is depicted in **Figure S3** and reveals that SnO<sub>2</sub> is the present species in the bulk phase.



Figure S2 a) SEM image revealing porous microscopic structure of GDE b) material

contrast image showing the homogeneous dispersion of tin catalyst on carbon support

c) MIP measurement of the GDE showing a bimodal pore-size distribution d) XPS

spectrum elucidating that SnO<sub>x</sub> is the dominating species on the catalyst surface.



Figure S3 Diffractogram obtained for the unsupported catalyst material revealing that

 $SnO_2$  is the present species in the bulk phase.



Figure S4 Difference plot of the imaginary parts for the a) current series whereas the

data obtained for - 50 mA cm<sup>-2</sup> are taken as reference **b)** temperature series whereas

the data obtained for 30  $^\circ\text{C}$  are taken as reference.

## Calculation activation energy E<sub>a</sub>

The activation energy  $\mathsf{E}_{\mathsf{a}}$  for the high – and medium frequency process was calculated

using the Arrhenius equation (Eq. S1).<sup>8</sup> R<sub>F</sub> represents the corresponding faradaic

resistance of the high - or medium frequency process. R<sub>F0</sub> represents the pre-

exponential factor. R is the universal gas constant whereas T represents the

temperature. The slope of the linearized Arrhenius equation (Eq. S2) includes the

desired information about the activation energy.

$$R_F = R_{F0} \bullet \exp\left(\frac{E_A}{R \bullet T}\right) \tag{S1}$$

$$\ln(R_F) = \ln(R_{F0}) + \frac{E_A}{R} \cdot \frac{1}{T}$$
(S2)

We did not want to perform equivalent circuit modelling (EQCM) to obtain the values for the faradaic resistances of the processes since it was not our aim to set up an equivalent circuit model. We focused on qualitative interpretation of our data since this is more convenient in the early stage of EIS analysis for CO<sub>2</sub>RR. However, to obtain meaningful Arrhenius plots we need the values for the resistances of the high- and medium frequency process. To get these values we calculated the polarization capacitance  $C_p$  via Eq. S3 for each spectrum of the temperature series.  $\omega$  describes the angular frequency. Z' and Z'' represent the real and imaginary part of the impedance.<sup>9</sup>,

10

$$C_{p} = \frac{1}{\omega} \cdot \left( \frac{-Z''}{(Z')^{2} + (Z'')^{2}} \right)$$
(S3)

The Z' values of the inflection points of the plot vs  $C_p$  vs. Z' mark significant changes of the time constants and by that dividing the spectrum into sections. The width of each section is the approximate resistance of the corresponding underlying process. Figure S5 exemplarily demonstrates the procedure for the spectrum obtained at 40 °C.



**Figure S5** - Nyquist plot obtained for the operation of the GDE at 40 °C and the corresponding plot of the polarization capacitance vs. Z'. The Z' values of the inflection

points divide the spectrum into section whereas the width of a section is the approximate resistance value for the underlying process.

The resistance values for the high- and medium frequency process for the tested temperatures are displayed in Table S1. These values are inserted into Eq. S2 and plotted (cf. Figure S6). The activation energy  $E_a$  for both processes was calculated via evaluation of the slopes of the lines.

 Table S1 Temperature dependent resistance values for the high- and medium

 frequency process.

Temperature / °C	30	30	40	40	50	50	60	60
R <sub>High frequency</sub> /	1.105	1.012	0.720	0.703	0.365	0.415	0.225	0.243

Ω								
R <sub>Medium frequency</sub> / Ω	1.646	1.624	1.284	1.408	1.108	1.014	0.982	0.884



Figure S6 Arrhenius plot for the high and medium frequency resistance for the

calculation of the activation energy for each process.



**Figure S7 a)** - Nyquist and **b)** imaginary part vs. frequency plot for a current series recorded during operation of the GDE with a feed gas composition of 20 vol%  $CO_2$  and 80 vol% N<sub>2</sub>. The diffusional arc in the low frequency domain vanishes at - 125 mA cm<sup>-2</sup> and the shape resembles the spectrum obtained for the operation with pure N<sub>2</sub>. This was interpreted as a change in the shape dominating reaction (from  $CO_2RR$  to HER) of the impedance spectrum.



Figure S8 - Nyquist plots obtained for H<sub>2</sub>O and D<sub>2</sub>O based electrolytes during operation

with pure **a**)  $N_2$  and **b**)  $CO_2$ . The total polarization resistance increases using  $D_2O$  based electrolyte for both gas feeds.

Comparison of EIS spectra obtained for CO<sub>2</sub>RR on tin foil and SnO<sub>x</sub> / C gas-diffusion

## electrode

For better classification we present a brief comparison of impedance spectra recorded for the operation with pure  $CO_2$  and  $N_2$  on tin foil and  $SnO_x$  / C gas-diffusion electrodes (cf. **Figure S9**). The detailed information regarding the spectra for tin foil electrodes can be found in a previous work of our group. <sup>11</sup>

It becomes evident when looking at the change of the spectrum for the GDE when substituting  $N_2$  with  $CO_2$  that the shape of the spectrum significantly changes from one

semi-circle to three semi-circles. As argued in the main text we suggested that this changing shape is due to a change of the shape-determining reaction from HER to  $CO_2RR$  because the resistance of the HER is increased during operation with  $CO_2$  while at the same time  $CO_2RR$  is favored evidenced by the faraday efficiency of 91% for the  $CO_2RR$ 

In comparison, EIS measurements for tin foil electrodes in N<sub>2</sub> and CO<sub>2</sub> saturated 1.0 M KHCO<sub>3</sub> solution showed two arcs. Importantly, the shape of the spectrum remains the same when N<sub>2</sub> is substituted with CO<sub>2</sub>. Merely the semi-circle diameters increase when CO<sub>2</sub> is used as feed gas suggesting that the shape-determining reaction is the same when operating the cell with CO<sub>2</sub> instead of N<sub>2</sub>. The fact that the spectrum shape for tin foil systems is in contrast to the GDE system independent of the feed gas might be explained due to the high HER faraday efficiency (FE H<sub>2</sub>: 87%) for CO<sub>2</sub> operation in the tin foil system. On the contrary, for the GDE system where the spectrum shape is dependent on the feed gas, the FE H<sub>2</sub> changes substantially from 100% for the operation with N<sub>2</sub> to 9% when operated with CO<sub>2</sub>.

The comparison between these two different electrode systems supports our theory that depending on the reaction conditions during  $CO_2RR$  the appearance of the EIS spectrum can change according to the more dominant and, therefore, shape-determining reaction during electrolysis. A distinct observed change in the spectrum shape does not necessarily have to be attributed to the alteration of properties describing the  $CO_2RR$  but can be ascribed to a change of the investigated (spectrum

shape-determining) reaction as well. Still, simple changes for the semi-circle diameters while maintaining the same impedance spectrum shape seem to be reasonable to evaluate the degree optimization or degradation of the investigated system.



Figure S9 Comparison of impedance spectra recorded for a) the operation of a GDE

with  $N_2$  and  $CO_2$  feed gas as shown in this contribution **b**) tin foil electrodes in  $N_2$  and

CO<sub>2</sub> saturated 1.0 M KHCO<sub>3</sub> as demonstrated in a previous work of our group.<sup>11</sup>

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