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COMMUNICATION

Electronic Supporting Information (ESI) for:

Quantitative *in situ* ^{13}C NMR studies of the electro-catalytic oxidation of ethanol

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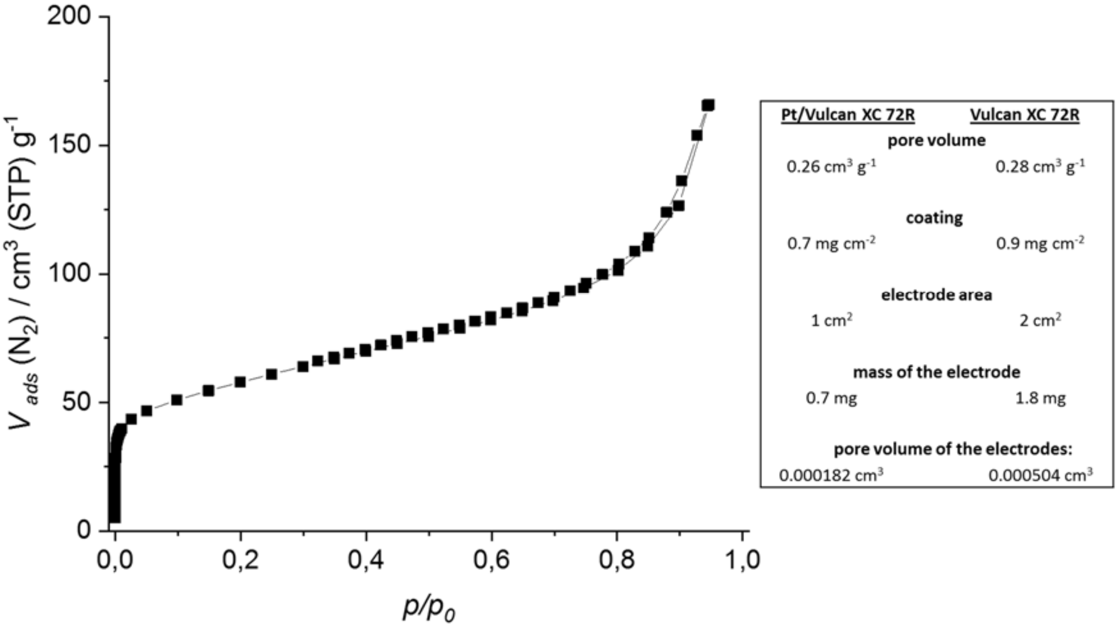
Characterisation of the catalyst

Nitrogen adsorption isotherms are used to characterize the pore volumes of the catalyst Pt/Vulcan XC 72R and the carbon Vulcan XC72R (Figure S1). Based on these measurements, the pore volumes were determined which are summarized in the insert of Figure S1. With these pore volumes, the absolute pore volumes of the electrodes could be calculated. These absolute pore volumes of the electrodes are very small in comparison to the electrolyte volume of the cell (500 µL). Therefore, detected products are mainly expected to be present outside the pores.



	Pt/Vulcan XC 72R	Vulcan XC 72R
pore volume	0.26 cm^3 g^{-1}	0.28 cm^3 g^{-1}
coating	0.7 mg cm^{-2}	0.9 mg cm^{-2}
electrode area	1 cm^2	2 cm^2
mass of the electrode	0.7 mg	1.8 mg
pore volume of the electrodes:	0.000182 cm^3	0.000504 cm^3

Figure S1: Nitrogen adsorption isotherm of the catalyst Pt/Vulcan XC 72R and description of the materials including specific and absolute pore volumes of the electrodes.

NMR experiments

Prior to the time-resolved *in situ* NMR measurements, an inversion recovery experiment with ethanol was accomplished under otherwise identical conditions to determine T_1. A value of 9 s was measured and a recycle delay of $5*T_1 = 45$ s was thus chosen. Comparative solid-state NMR measurements on the carbon Vulcan XC 72R soaked with electrolyte were performed with and without MAS (magic angle spinning). This comparison revealed that the line broadening without MAS is decent compared to the MAS signals and allows resolution and quantification of the signals due to ethanol and its oxidation products.

Measurement without pressure release

Measurements on pouch cells without pressure release (i.e., without opening with a needle on the top) indicate a significantly decreased turnover of ethanol in comparison to a pouch cell with the described small perforation. This is clearly visible from the comparison of Figures 2 and S2. The measurement of a fully sealed pouch cell shows a much different product spectrum in comparison to an opened pouch cell. Neither carbonate nor acetaldehyde nor the other intermediates found in Figure 2 are present in Figure S2. Only a minor amount of acetic acid is formed. The reaction completely stops after short reaction times of about 2 hours. Visual inspection of the pouch cell after the experiment revealed an overpressure which demonstrates the tightness of our cells before opening. That means, electro-oxidation may be inhibited by the presence of the overpressure due to carbon dioxide formation. Another reason for this behaviour could be the need of oxygen from air for the oxidation reaction. Generation of the active oxygen species takes place at the counter electrode. This is necessary for the oxidation reaction.[1] In a closed pouch cell, the oxygen for the oxidation reaction is limited and the electro-catalytic ethanol oxidation may thus be inhibited due to this limitation.

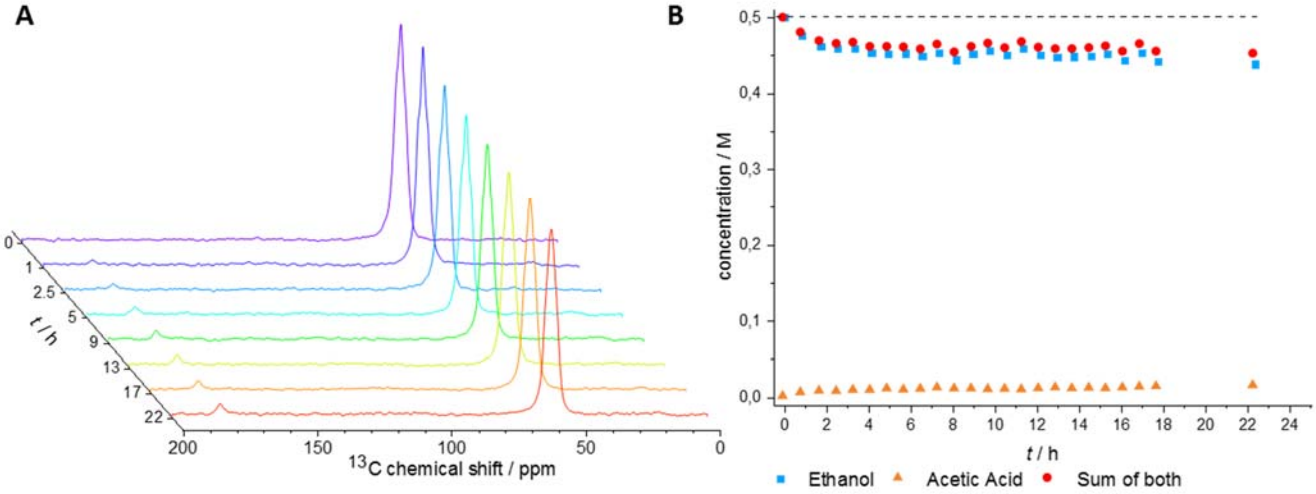


Figure S2: *In situ* ^{13}C NMR measurements of a closed pouch cell at 1.3 V. **A** *In situ* ^{13}C NMR spectra measured as a function of reaction time. **B** Quantification of spectra.

Measurements at variable voltage

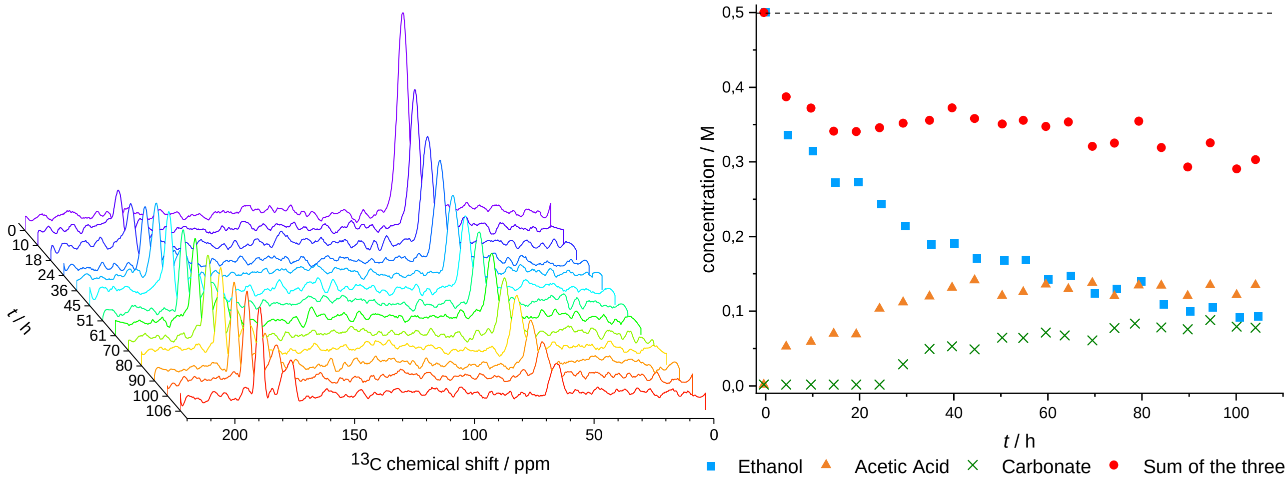


Figure S3: *In situ* ^{13}C NMR measurements at 1.0 V: **A** *In situ* ^{13}C NMR spectra measured as a function reaction time. **B** Quantification of the spectra.

The applied voltage strongly influences the reaction rate of ethanol oxidation and the product spectrum (cf. Figure 2, S3, and S4). The conversion of ethanol at 1.0 V (Figure S3) takes much longer than at 1.7 V (Figure S4). Conversion of ethanol at 1.0 V leads to the formation of acetic acid and carbonate. However, there is still some ethanol present in the cell even after 100 hours. Formation of carbonate is first observed after 35 hours. Before, mainly carbon dioxide must thus be formed. In comparison, the experiment at 1.7 V initially shows a signal due to carbonate within the first 10 hours. Afterwards, the carbonate signal decreases and finally disappears after approx. 35 hours. The decreasing carbonate signal could be explained by the transformation of carbonate into carbon dioxide which is volatile and can escape from the opened cell. Additionally, carbonate can adsorb very strongly at the catalyst surface.[2] This may lead to strong line broadening preventing the signal detection. After 10 hours and later, acetic acid is detected as the main product. After about 70 hours, almost complete conversion of ethanol is found. In summary, it is obvious that turnover rate and product spectrum clearly depend on the applied voltage.

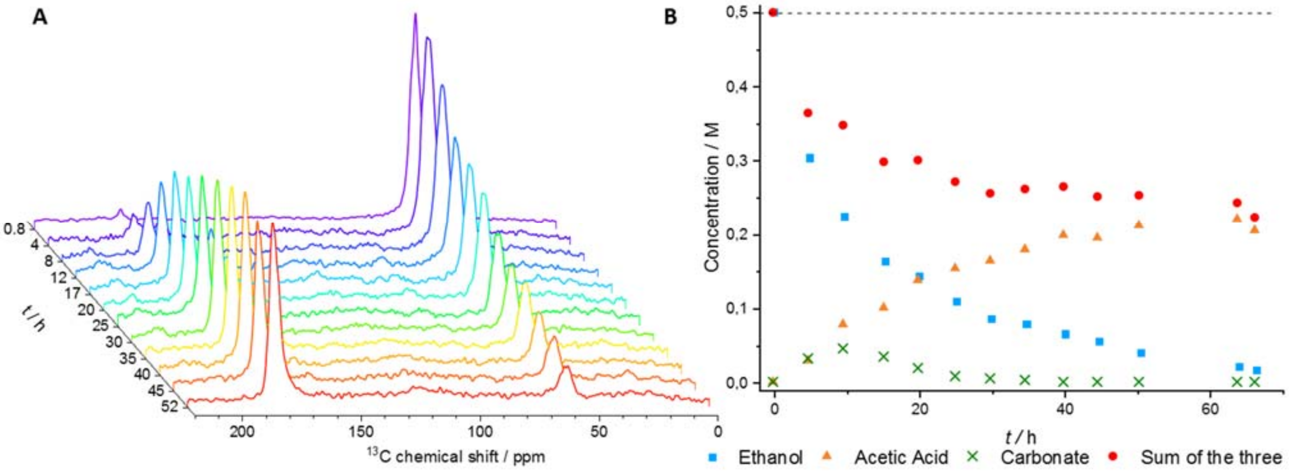


Figure S4: *In situ* ^{13}C NMR measurements at 1.7 V: **A** *In situ* ^{13}C NMR spectra measured as a function reaction time. **B** Quantification of the spectra.

Notes and references

1 An, L.; Zhao, T. S., *Energy Environ. Sci.,* 2011, **4**, 2213.
2 J. S. Spendelow and A. Wieckowski, *Phys.l Chem. Chem. Phys.*, 2007, **9**, 2654.