Supporting information

Average half cell potentials vs. currents

Figure S1 shows the average iR-corrected half-cell potentials for different operating current densities, calculated as:

$$E_{iR} = E_{vs.\ Ag/AgCl} + 0.2\ V + 0.059 \times pH - iR$$

where R is the electrolyte resistance with a value of $5.3 \pm 0.6\ \Omega$, $E_{vs.\ Ag/AgCl}$ is the measured potential vs. a reference Ag/AgCl reference electrode, i is the set current and pH is the initial pH of the electrolyte
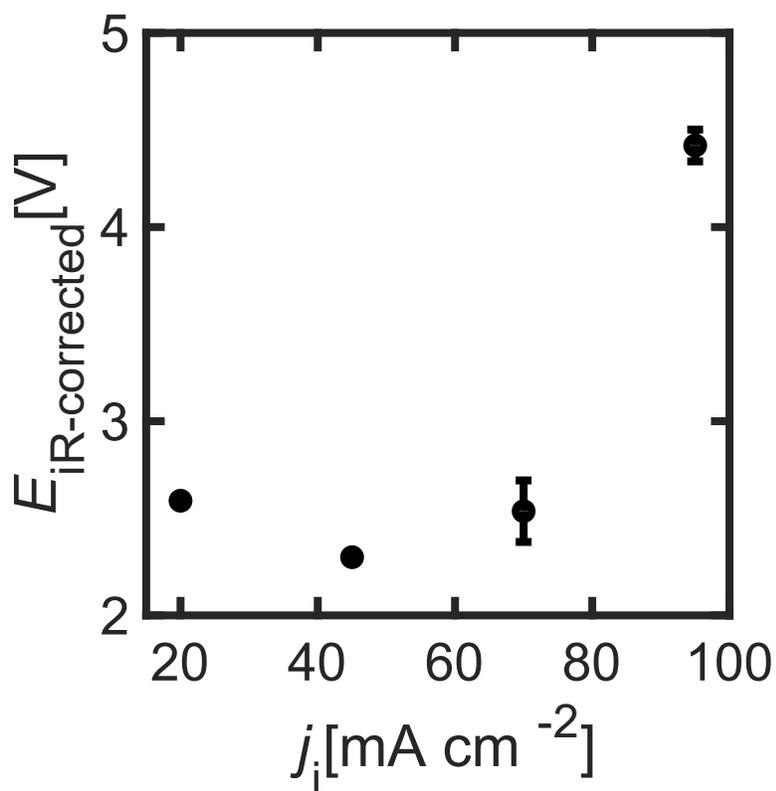
Figure S1. Average half cell potentials iR-corrected under different operating current densities.

Solution resistance measured through EIS was $5.3 \pm 0.6 \, \Omega$

Electrolyte temperature variation during experiments

From Figure S1, it is evident that from 20 to 45 mA cm^{-2} the half-cell potential slightly decreases, which can be possibly due to the significant pH decrease during the reaction or due to an increase in electrolyte temperature due to a thermal effect which is more pronounced at higher temperatures. To that end, Figure S2 shows the reaction temperature as a function of time for the different current densities evaluated, as well as the half-cell potential
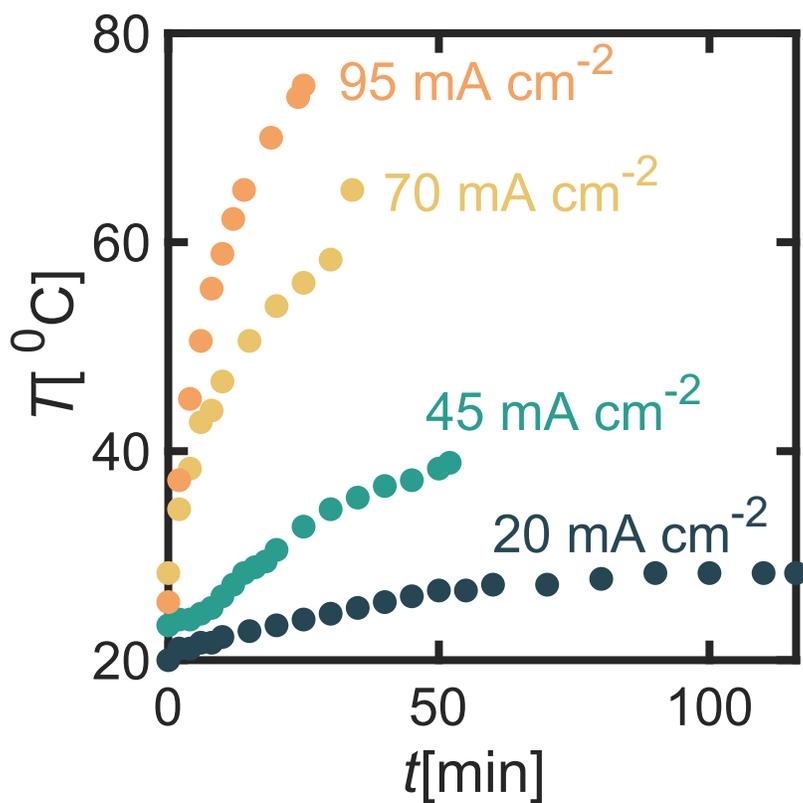
Figure S2. Electrolyte temperature during electrochemical reaction for j of 20, 45, 70 and 95 mA cm^{-2}. Electrolyte was 0.5 M Na$_3$PO4, [PA]$_0$ 2 M, pH$_0$ 7

Production rates (R_i) calculations:

Production rates were calculated as follows:

$$R_i = \frac{FE_i j}{Fz_i}$$

Where R_i is the production rate of the ith species with unis of [mol cm^{-2} h^{-1}], FE_i is the faradaic efficiency with units of [A], F is Faraday's constant with units of [A h mol^{-1}] and z_i is the number of electrons transferred to produce one molecule of the species i.

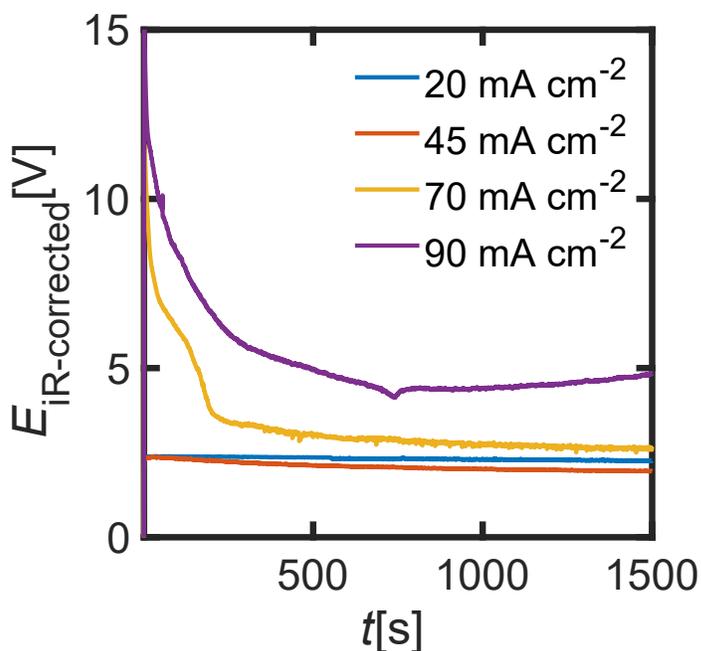**Cell potential stability over time**

Figure S3. iR-corrected potential traces over time for the 4 current densities studied. [PA]$_0$ = 2 M, electrolyte pH$_0$ was 7 ± 0.2. The reaction volume was 14. Experiments performed in a divided H-

Cell, using Nafion® as a proton exchange membrane min at ambient temperature without temperature control. Electrolyte was Na_3PO_4 0.5 M. The reaction time of each experiment was selected to maintain the total charge transferred constant for the different current densities, and they were 116, 52, 34 and 25 min for $j = 20, 45, 70, 95$ mA cm^{-2} respectively. A cold trap was implemented downstream of the gas effluent to condense any liquid products evaporated during the reaction.

Acetic Acid H-NMR quantification – adjustment

When analyzing solutions of propionic acid in deionized water using H-NMR, acetic acid was detected as a contaminant, which presented a challenge during product analysis since acetic acid is one of the possible products of propionic acid electrooxidation (Figure S4).
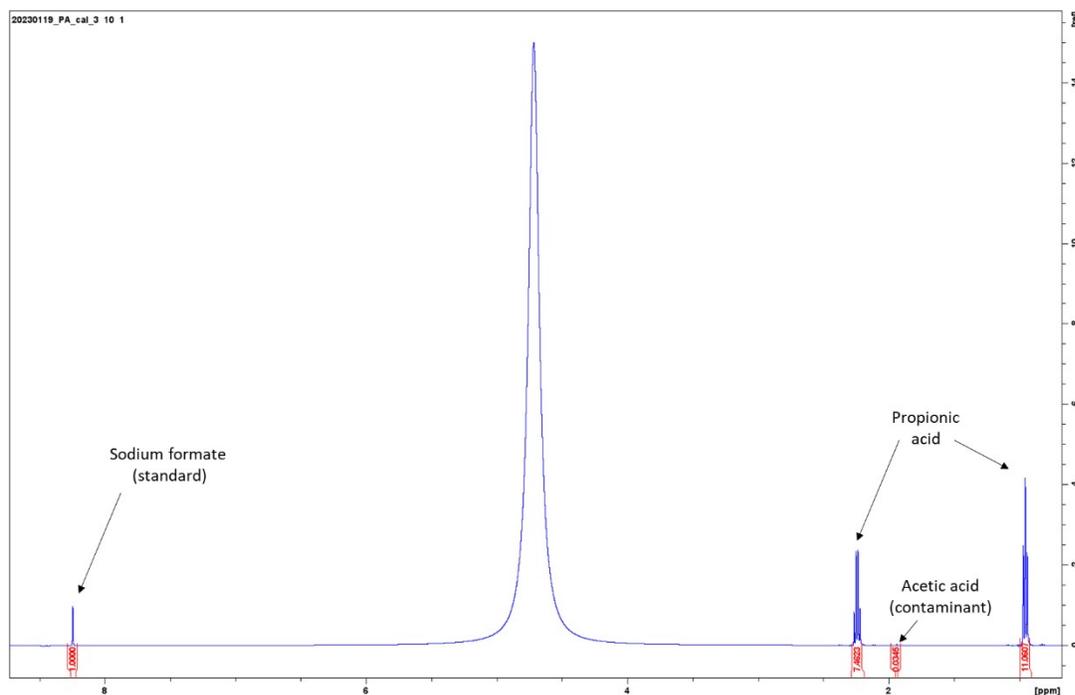
Figure S4. H-NMR spectrum of a 1.1 M propionic acid solution, with trace amounts of acetic acid (singlet @ 1.9 ppm). Estimated 3×10^{-3} mol acetic acid per 1 mol of propionic acid

To circumvent this issue, we subtracted from the acetic acid singlet peak area, the area corresponding to the concentration of acetic acid present in the initial solution due to the contamination of our substrate. The estimation was performed as follows:

$$A_{AA, real} = A_{AA, measured} - A_{AA, cont}$$

$$A_{AA, cont} = 0.0152 * [PA]_0$$

Where $A_{AA, real}$ is the estimated area of the singlet peak corresponding to the amount of acetic acid produced during the electrooxidation, $A_{AA, measured}$ is the measured area of the acetic acid peak during H-NMR analysis, $A_{AA, cont}$ is the contaminant contribution to the measured area of the acetic acid peak and $[PA]_0$ is the initial concentration of propionic acid. The relation (S.2) was determined empirically.

Control experiments to assess the production of ethyl propionate via the esterification of propionic acid and ethanol (non-electrochemical).

To assess whether ethyl propionate can form due to the esterification reaction between the PA and ethanol, we performed control experiments in which we added a PA (2 M) and ethanol (0.05 M) solution to our reactor without passing any current and after 52 min analyzed the solution. We evaluated two temperature conditions, first at room temperature and secondly controlling the temperature at 40 ^{0}C to simulate the reaction conditions more closely. During these conditions, no ethyl propionate was detected, which suggests that the ester is formed via the reaction of the

deprotonated acid and the ethyl cation formed electrochemically. Figures S5 and S6 show the H-NMR spectra of the resulting solution under both temperature conditions.
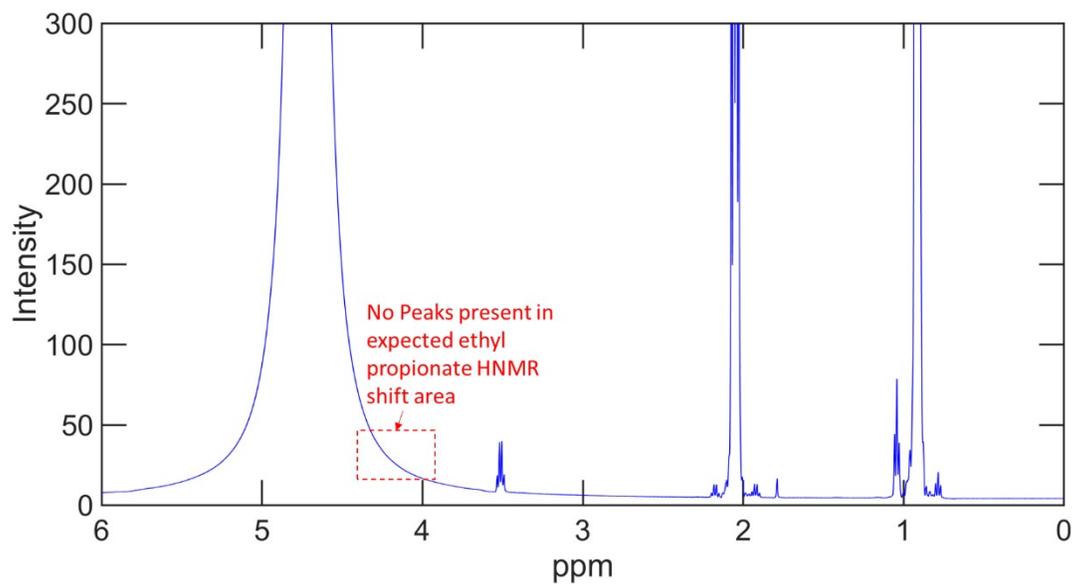

Figure S5. H-NMR plot of reactor solution with no current after 52 minutes of mixing at room temperature.
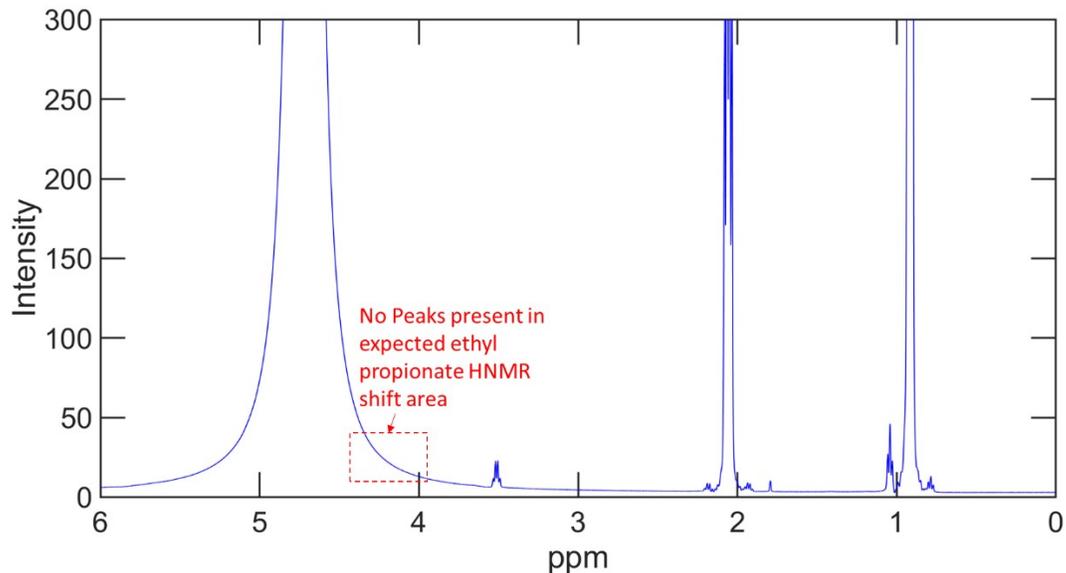
Figure S6. H-NMR plot of reactor solution with no current after 52 minutes of mixing at 40 degrees Celsius.

Control experiment to assess the production of ethane via the hydration of ethylene (non-electrochemical)

The possible formation of ethanol via the hydration of ethylene was studied by bubbling ethylene gas into the electrolyte solution and performing H-NMR analysis. After 52 min of bubbling ethylene at a rate of 10 sccm, no ethanol was detected. The resulting H-NMR spectra is shown in Figure S7.
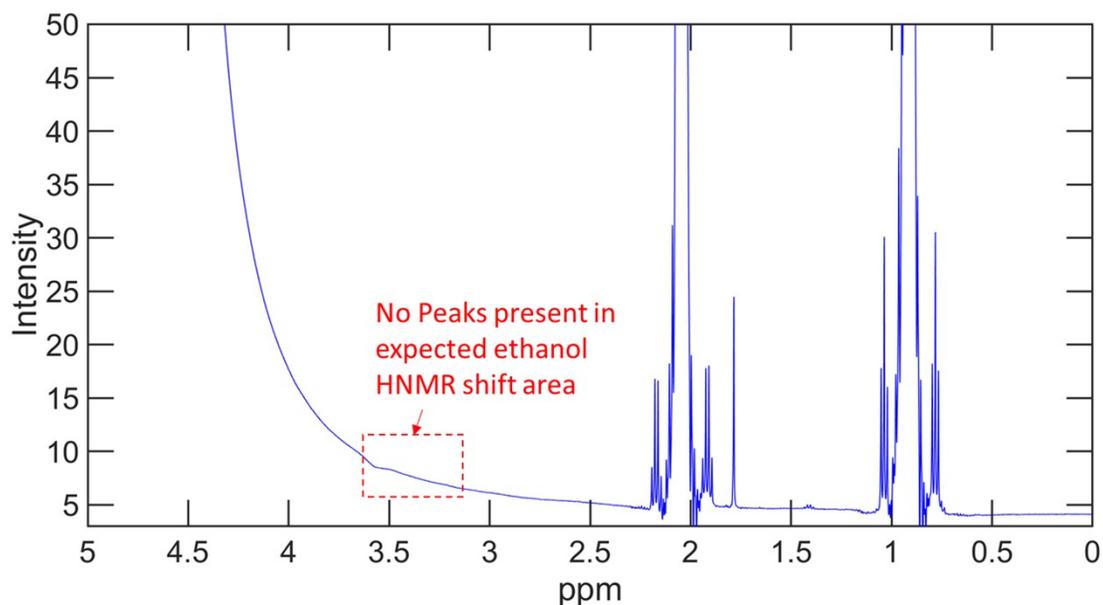
Figure S7. H-NMR plot of reactor solution after 52 minutes of 10 sccm ethylene bubbling.

Effect of electrolyte temperature in product distribution

Temperature can influence the reaction kinetics and product distribution. We performed a temperature-controlled experiment by surrounding our reactor with a heated sand bath (60 °C) the reaction time and analyzed the faradaic efficiency for all products. A change in the distribution of products was observed; with the use of a heated sand bath, the FE of oxygen increased from 5% to 20 %, while the FE for ethylene and ethanol decreased from 52% to 42 % and from 25% to 19% respectively (Figure S8). Developing a scalable process based on this reaction would require careful consideration and control of the reactor temperature to achieve consistent product distributions.
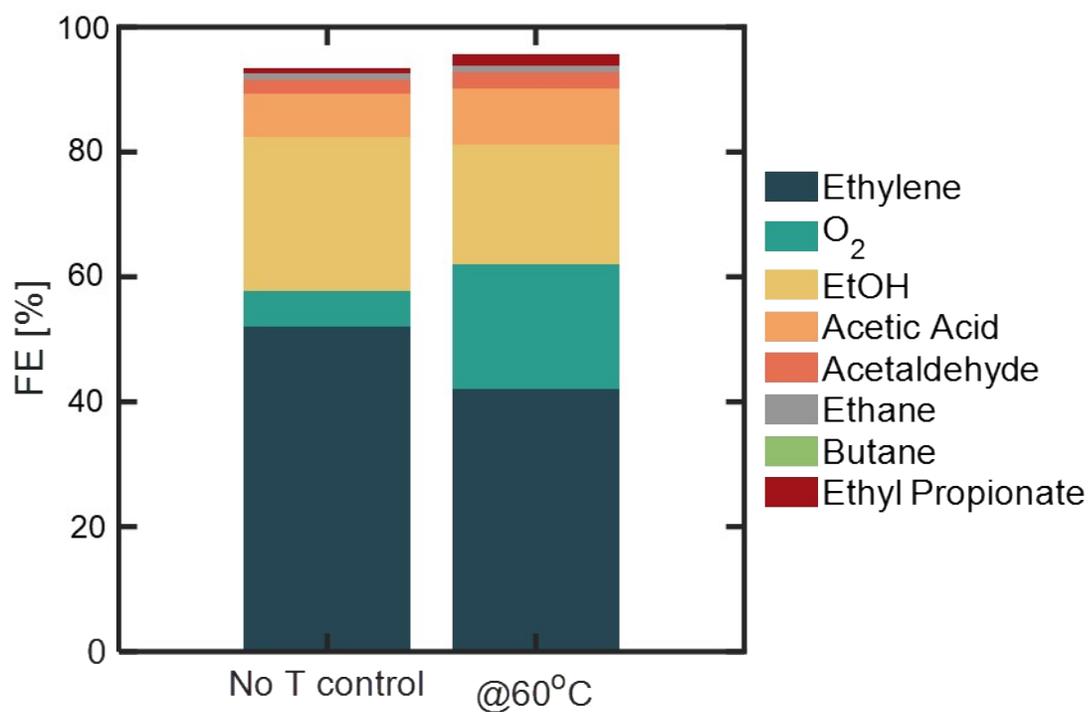
Figure S8. FE of electrochemical products generated from 45 mA cm^{-2} without temperature control and under 60 degrees Celsius environment for 2M PA with pH of 7.

Representing H-NMR spectra containing signals corresponding to ethyl propionate, ethanol, and acetaldehyde.

Figure S9 shows a sample spectrum where ethyl propionate, ethanol and acetaldehyde were detected and quantified via H-NMR spectroscopy. The sample was collected from the cold trap incorporated downstream of the reactor gas outlflow.
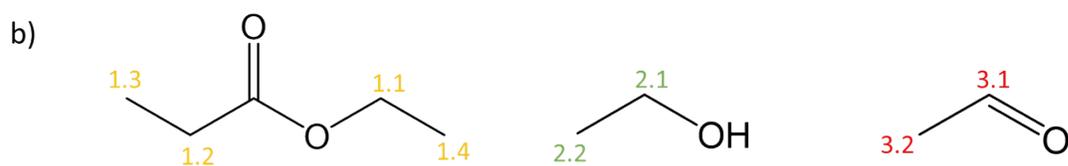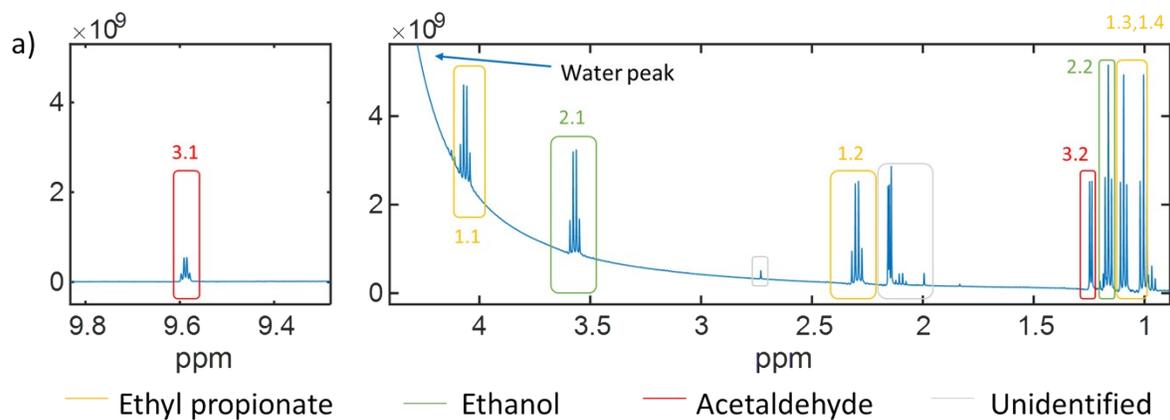
Figure S9. a) H-NMR spectrum from a selected experiment where the presence of ethyl propionate, ethanol and acetaldehyde is observed. The spectrum corresponds to a sample pulled from the cold trap downstream the reactor's gas purge outlet (hence the absence of PA). Reaction was performed at 90 mA cm^{-2}, $[PA]_0$ = 2M, pH_0 = 7, at ambient temperature, reaction time of 25 min. Selected sections with the signals of interested are shown, entire spectrum provided in the online repository. b) Molecular structures of ethyl propionate, ethanol and acetaldehyde with labeled group of protons.