

Supplementary Information

Oxygen-Enhanced Chemical Stability of Lithium-Mediated Electrochemical Ammonia Synthesis

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Experimental Methods

Electrochemical ammonia synthesis

All the electrochemical experiments were conducted in a 3-electrode single compartment glass cell placed in a home-built electrochemical autoclave inside an Ar glovebox. The setup is shown in Figure S1. The regular electrolyte solution was prepared in an inert argon-filled (Ar) glovebox from 0.3 M LiClO₄ (Battery grade, Sigma Aldrich) in 99 vol. % tetrahydrofuran (THF, anhydrous, inhibitor-free, Sigma Aldrich) and 1 vol. % ethanol (EtOH, anhydrous, Honeywell). As a working electrode (WE), molybdenum (Mo) foil (+99.9 %, 0.1 mm thick, Goodfellow) attached by spot-welding to a Mo wire for electrical contact was used. The WE was cleaned in 2% HCl (VWR Chemicals), rinsed in ultra-pure water (miliQ, 18.2 MΩ cm⁻¹) and EtOH and polished with SiC paper (CarbiMet, Buehler). Afterwards it was again rinsed in EtOH and dried before usage. The counter electrode (CE) was made of a platinum (Pt) mesh (99.9 %, Goodfellow), and the reference electrode (RE) was a Pt wire (99.99 %, Goodfellow). The CE and RE were boiled in ultra-pure water (miliQ, 18.2 MΩ cm⁻¹), dried overnight at 100 °C and finally flame-annealed before the experiments. The single compartment glass cell and a magnetic stirring bar (VWR, glass covered) are boiled in ultra-pure water, washed with EtOH for 3 times and dried overnight at 100 °C in air. The WE and CE are ~0.5 cm apart, and the surface area of the WE facing the CE is 1.8 cm_{geo}². The cell is brought into the glovebox straight from the oven while it is still hot, to limit H₂O sticking to the walls. The electrodes are mounted in the cell, and it is placed inside the autoclave in the Ar atmosphere of the glovebox, and the autoclave is closed off. The N₂ (6.0, Air Liquide) and synthetic air (20 % O₂ in N₂, 6.0, Air Liquide) used in the experiments was additionally cleaned

by purifiers (NuPure, pptV impurities of H₂O and N-containing contaminants removed). To set the molar ratio of O₂ in N₂ the flow of the N₂ and synthetic air was adjusted with mass flow controllers (Brooks). The pressure in the autoclave was increased to 10 bar and de-pressurized to 3 bar 10 times with the gas mixture in order to remove any remaining Ar. Afterwards, the setup was filled with O₂/N₂ to 20 bar for the main experiments, and the ratio of gasses were measured using a micron-sized orifice and a mass spectrometer (Pfeiffer Vacuum, OmniStar™, Gas Analysis System). The system was usually left for 20 min at open circuit potential to allow the gasses to equilibrate. The electrolyte was stirred at 250 rpm throughout the whole experiment to increase the mass transport in the system and triple-phase boundaries (gas-liquid-solid). The electrochemical experiments included the potentiostatic electrochemical impedance spectroscopy (PEIS) to determine the resistance in the electrolyte, a linear sweep voltammetry (LSV) from open circuit voltage (OCV) until clear and distinct lithium ion reduction, and a chronopotentiometry (CP). After CP, another PEIS was run to ensure the changes in the resistance. The LSV was run before CP in every experiment to determine the Li reduction potential scale, and the values were reported versus platinum pseudo reference electrode (Pt_{pseudo}). During CP, a steady current density of -4 mA/cm² is used for all the experiments. It is important to note that all experiments were conducted at ambient temperature in summer. Consequently, the FE values obtained are lower compared to the values previously reported in our group¹⁻⁴ due to the increase in temperature (measured to be ~40 C with thermocouple in the glovebox),, which is detrimental to the reaction since nitrogen solubility is inversely proportional to the temperature. After all the LiMEAS experiments the electrolytes were colorless and transparent and did not change in time.

Quantification of ammonia

In all the experiments, the synthesized ammonia (NH_3) was quantified by a modified colorimetric indophenol method, previously described.⁵ As has previously been reported,⁶ the GCMS could be used to evaluate the concentration of NH_3 in the electrolytes after LiMEAS. However, the specially designed program has to be applied to the ex situ measurements. The sample absorbance was analyzed by ultraviolet-visible light (UV/Vis) spectroscopy using UV-2600 (Shimadzu) spectroscope in the range 400-1000 nm. The blank background solution was subtracted from each spectrum, and then the difference in absorbance at the peak around 630 nm and through around 860 nm is used. A fitted curve of the difference between the peak and trough of each concentration showed a linear regression with an R^2 value of 0.998. This method is more advantageous opposed to the more common peak based methods because long-time experiments might have solvent breakdown, which can give a falsely high peak at the ammonia wavelength, due to interference from the evolved solvent mixture background. For each measurement, 4 samples of 0.5 mL were taken from the electrolyte. One sample from the electrolyte is used as a background, and the mean and standard deviation of the remaining 3 samples is reported as error bars in Figure 3c. The remaining samples were treated as described previously⁵⁻⁶, to determine the NH_3 concentration. In the case when the expected concentration of NH_3 exceeds the concentration limits of the indophenol method, the sample is accordingly diluted with ultra-pure water after drying.

Gas chromatography – mass spectrometry (GCMS)

All of the gas chromatography-mass spectrometry (GCMS) measurements in this study were done with an Agilent 6890N gas chromatograph with manual liquid sample injection. All the samples

were analyzed immediately after LiMEAS by injecting each of them (0.1 μL) to an inlet at 200 $^{\circ}\text{C}$ and electron-ionized with 30 eV in order to form positive ions (e.g., M^+). The injection volume of 0.1 μL was optimized to get reliable intensities of the peaks without overloading the detector. As a carrier gas, helium (N5.0 purity, Air Liquide) was used with 5 mL min^{-1} flow through the column and 5 mL min^{-1} purge flow. As a filter and collector, a cotton fiber in the inlet was used to avoid deposition of lithium perchlorate (LiClO_4) or any other non-volatile species present in the electrolyte in the column upon evaporation of the injected liquid sample. The setup of 2 columns connected in series was used in this study: a non-polar Agilent CP-Volamine (30 m x 0.32 mm x 0.32 μm) and non-polar Agilent HP-5MS UI (30 m x 0.32 mm x 0.25 μm). The temperature program is represented in Figure S4. The GCMS experiments started at 50 $^{\circ}\text{C}$ which was held for 3 min. The ramping of the temperature with 10 $^{\circ}\text{C min}^{-1}$ until 100 $^{\circ}\text{C}$ was performed with dwell time at each temperature of 1 min. The temperature was held for 3 min at 100 $^{\circ}\text{C}$, then ramped to 120 $^{\circ}\text{C}$ with 20 $^{\circ}\text{C min}^{-1}$, held for 1 min, ramped to 150 $^{\circ}\text{C}$ with 30 $^{\circ}\text{C min}^{-1}$. Finally, the system was heated to 190 with 40 $^{\circ}\text{C min}^{-1}$, held for 3 min, and cooled down to room temperature. The overall measurement time was around 25 min screening the mass range from 1–200 m/z with an event time of 0.1 s in scan mode. It is very important to mention that before the GCMS experiments, the blank electrolyte was injected in order to check for there was any in situ decomposition reactions in GCMS. No volatile compounds except the components of the electrolyte were detected –the initial electrolytes were clean with no side reactions in the hot GC inlet.

EI-MS Analysis

The GC was interfaced with a sector mass spectrometer (Autospec v4.0 mass spectrometer, Waters Corporation). A very high mass resolution of ~ 30000 and mass accuracy of 1–2 ppm were achieved. Initially, the chromatograms and mass spectra were monitored and analyzed with MassLynx v4.0 (Waters Corporation) software. The mass spectrometer was run in the electron impact ionization (EI) mode with the following parameters: the temperature of the ion source together with the GC inlet was set to 200 °C, and the filament was operated at a voltage of 30 eV. The detector voltage was set relative to the respective tuning results. Compound identification and corresponding structural formulae were assigned relying upon the National Institutes of Standards (NIST) library⁷ and most of them including the more detailed description were reported previously.⁶ A full scan mode ranging from m/z 1 to 200 was applied to the instrument. The compounds were confirmed with their retention time and fragment patterns of in-house made standards from commercially available compounds (Sigma Aldrich). The compound of 100 ppm was dissolved in THF and injected into GCMS. Before each run, a mixture of ethanol and THF was used to rinse the lines and analyzed at the same time to generate a background spectrum. Every recorded GCMS data set was processed and mass-by-mass analyzed in order to evaluate the molecular masses of the molecular ions and fragmentation patterns using the OpenChrom and MassLynx 4.0 software. As the initial data, the total ion current (TIC) chromatograms were collected. However, each sample was thoroughly analyzed by m/z values as extracted ion chromatograms (XIC or EIC). In a reconstructed-ion chromatogram (RIC), one or more m/z values of interest are recovered taken and represented in time from the entire data set for a chromatographic run,⁸ revealing species if any at specific retention time of the chromatograms,

which were not visible in TIC. The total sum intensity, in other words called the base peak intensity, within a mass tolerance range of interest around m/z of a particular compound is plotted at every point in the analysis. The size of the mass tolerance range typically depends on the mass accuracy and mass resolution of the data collecting instrument. XIC is generated by focusing upon the ions of interest with specific m/z in the whole data set containing the full mass spectrum over time after the fact. More discussion on the methods is given elsewhere.⁶

The area of the most intense XIC fragment of the eluting compound was integrated and compared to the main peaks of THF and EtOH. After integration, the relative amount of compound was estimated and compared to the appropriate in-house made 100 ppm concentration standard in THF. The integration of the XICs method for other compounds is in a good agreement with the experimental standards and confirms the evaluated amount of the compound molecule. Further description of the method is given elsewhere.⁶

The GCMS data was analyzed with super user-friendly open source software OpenChrom.⁹ It is highly recommended for all the GCMS users.

NMR Analysis

The NMR spectra were acquired using an AVANCE III HD 400 MHz spectrometer equipped with a 5 mm Prodigy probe with either deuterium oxide (D_2O) or deuterated chloroform ($CDCl_3$). Prior to NMR, the electrodes were kept in the Ar-filled glovebox overnight. In addition, the reference THF+EtOH represents the 1 vol% EtOH solution in THF, and contains 4 main peaks belonging to different protons of EtOH and THF. The proton on the oxygen is drifting and might not be seen in

general in the spectrum. As can be seen from Figure 4, this was enough to get rid of all the THF and EtOH. All the chemical shifts of the samples were normalized to tetramethylsilane (TMS). The very little variation of chemical shift of the NMR signals could appear due to slight differences in the pH, volume, and/or temperature of the samples. The data was analyzed with Topspin 4.0.8 software. The concentration of the material from the surface of the WE was very small in order to obtain ^{13}C NMR spectrum. However, the latter is not useful in the specific application of this study with organic multicomponent systems from multicomponent electrolytes and surfaces of the electrodes. ^{15}N NMR spectrum was recorded additionally, however did not reveal any additional information.

Faradaic efficiency calculation

In order to calculate the Faradaic efficiency (FE), the molar concentration, c_{NH_3} (mol L^{-1}), of synthesized NH_3 in the electrolyte is measured via an indophenol colorimetric UV/Vis along with the total electrolyte volume, V (L), after each electrochemical measurement, and is compared to the total charged passed, Q :

$$FE_{\text{NH}_3} = \frac{3 \cdot F \cdot c_{\text{NH}_3} \cdot V}{Q} \quad (1)$$

where F is Faraday's constant of 96485 C mol^{-1} , and the number 3 represents the electrons transferred during the reaction for each mole of NH_3 as shown in the following equation,



Figures and Images

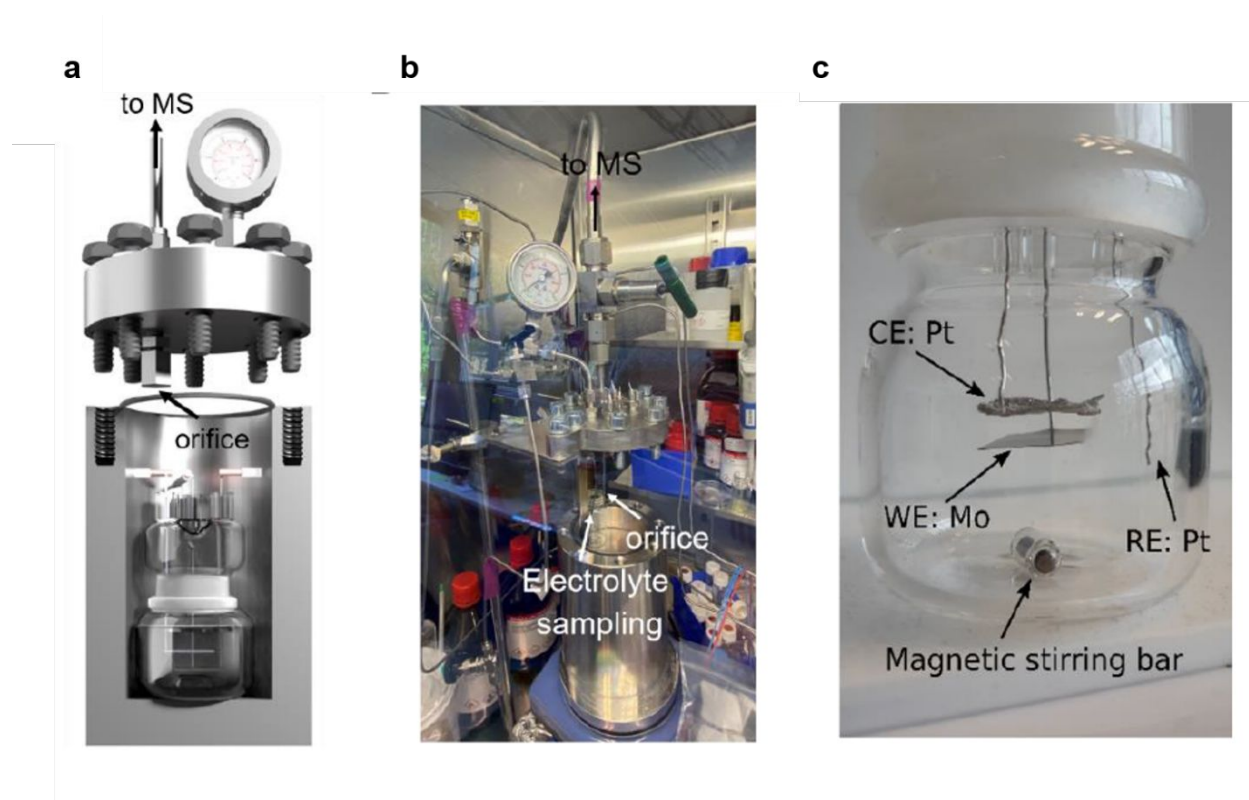


Figure S1. The setup of the glass cell and autoclaves: (a) 3D model and (b) real life image of the autoclave in an Ar glovebox used for the experiments. (c) A glass cell with three electrodes, WE, CE and RE, assembled for the measurements.

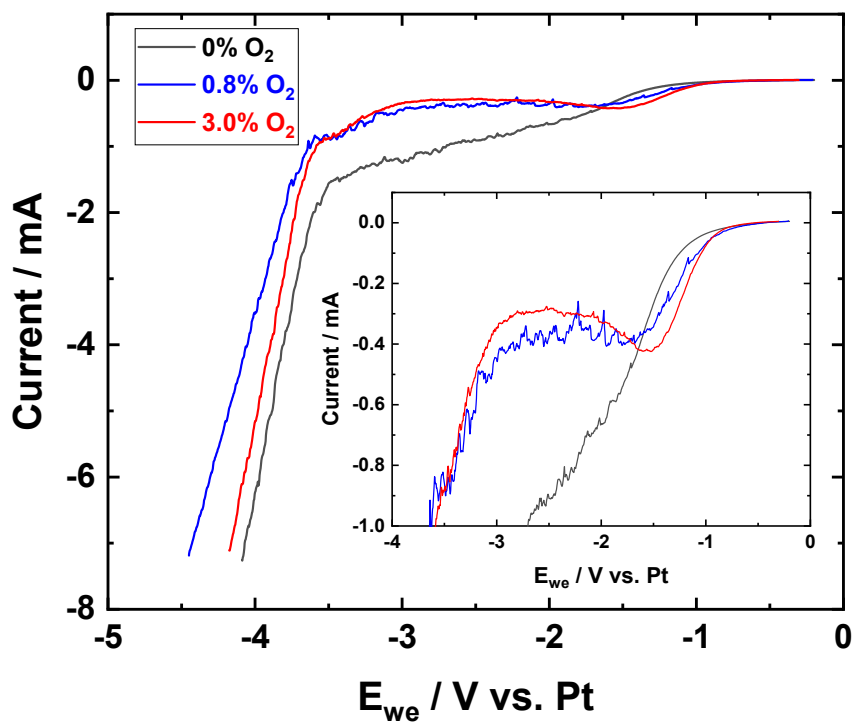


Figure S2. The linear sweep voltammograms (LSV) of LiMEAS with different oxygen content before chronopotentiometric (CP) analysis.

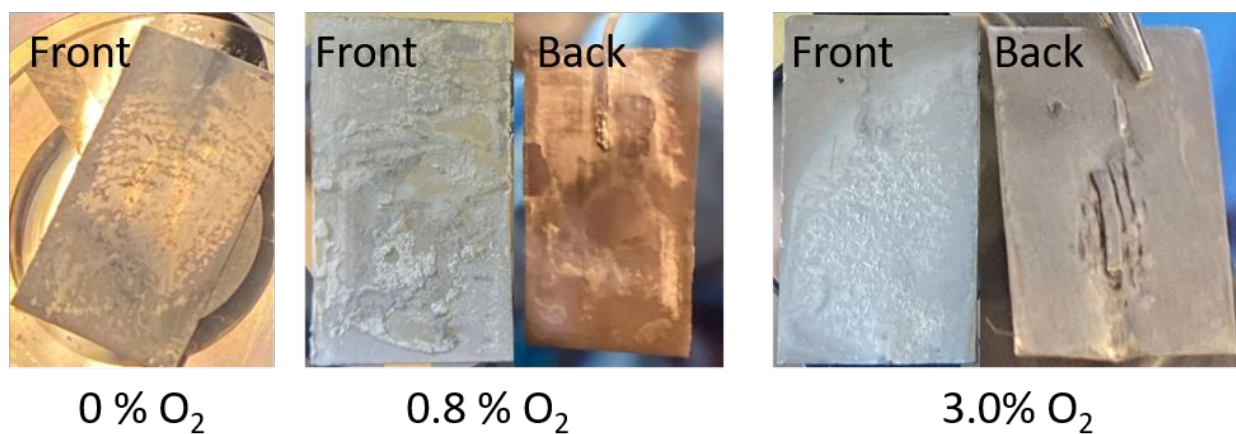


Figure S3. The images of the electrodes after LiMEAS dried in the inert (Ar) atmosphere glovebox with different concentration of O_2 added to the system.

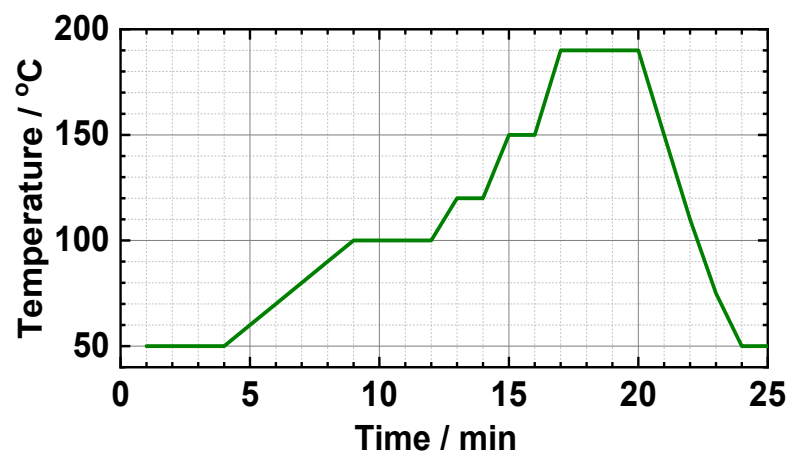


Figure S4. The GCMS temperature program used for the analysis of the electrolytes after LiMEAS with different oxygen content.

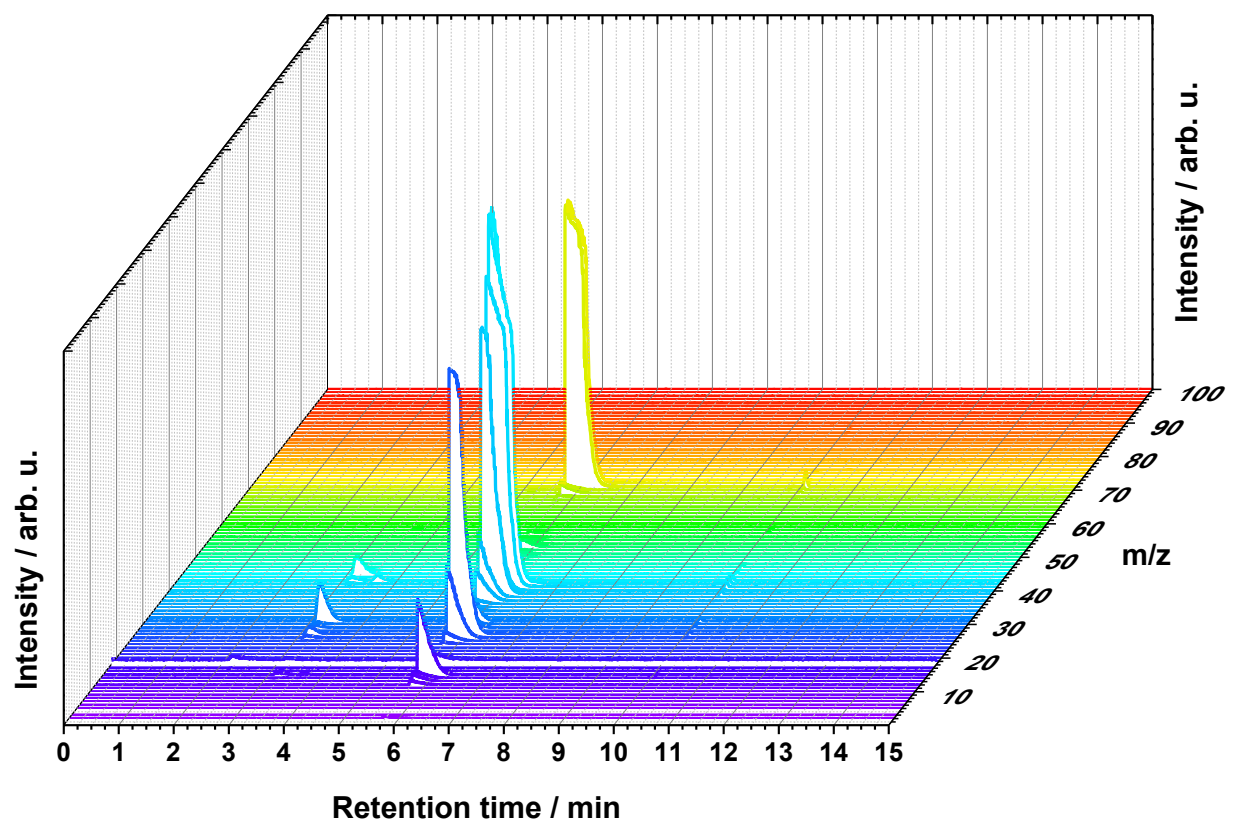


Figure S5. The full 3D chromatogram of the electrolyte after LiMEAS with optimal 0.8 mol% O₂ added to the system.

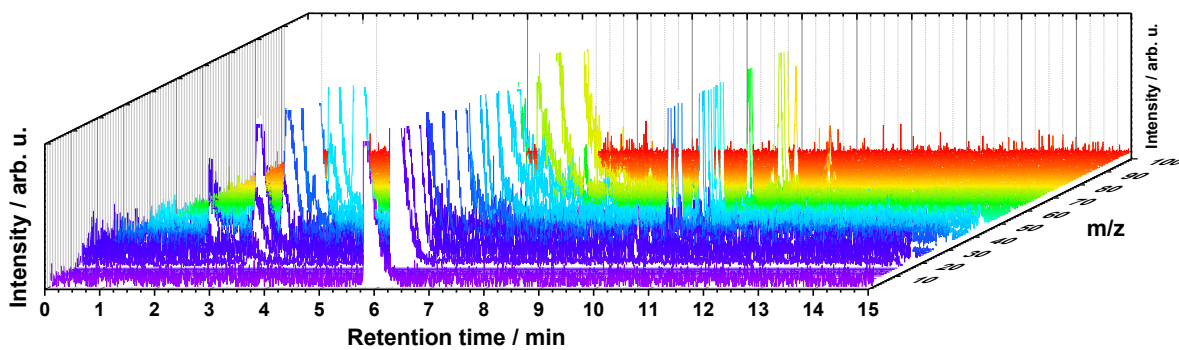


Figure S6. The 3D GCMS chromatogram magnified in Y-direction of the electrolyte after LiMEAS with optimal 0.8 mol% O₂ added to the system.

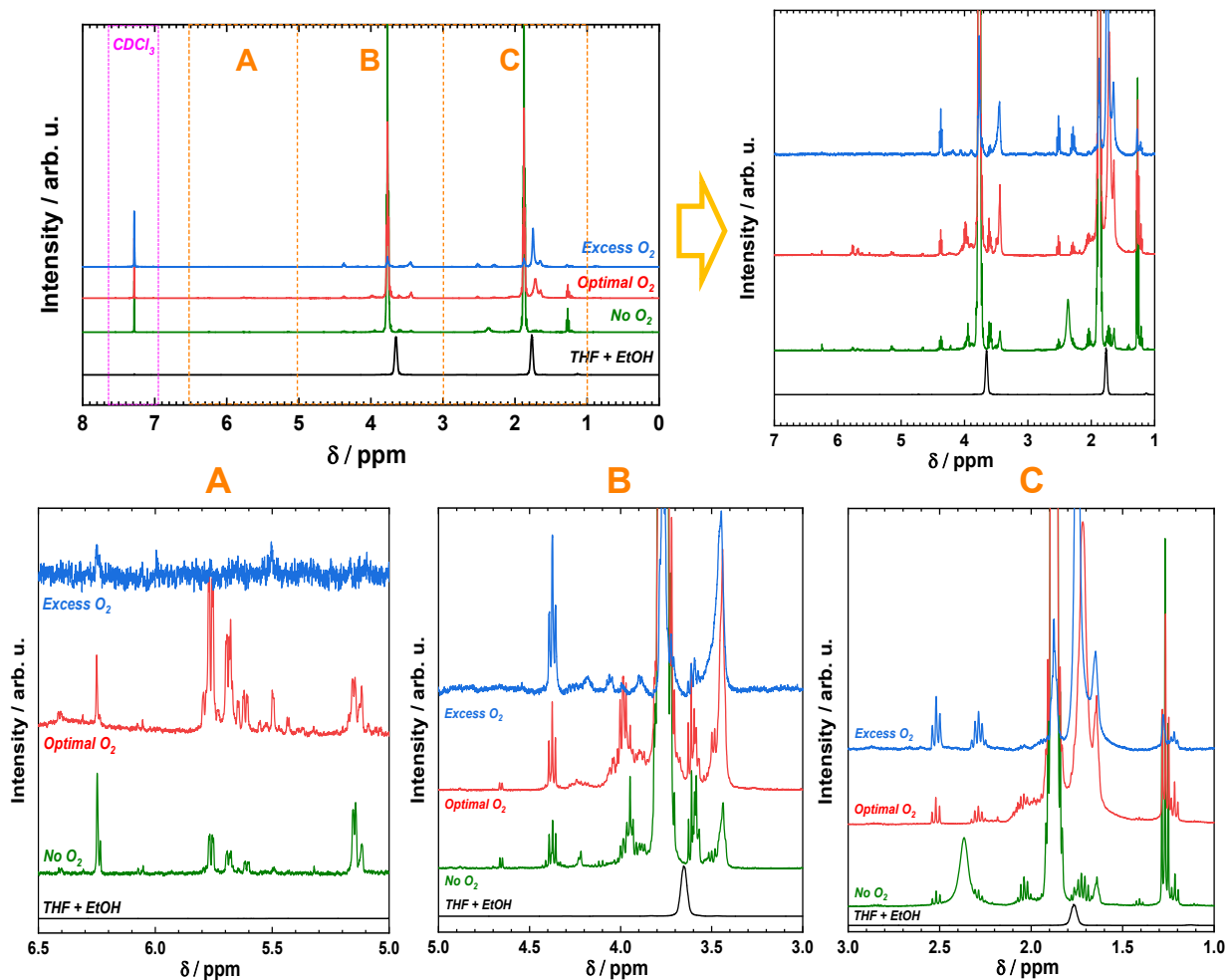


Figure S7. The ¹H NMR results of the electrolyte after drying at 60 °C from THF/EtOH and the residue dissolved in CDCl₃ after LiMEAS with different O₂ concentration. A, B, and C represent selected regions in the spectrum.

Tables

Table S1. The results for quantification of decomposition products after LiMEAS with 0 mol% O₂ in THF-based electrolyte. The main product is highlighted in bold.

| Nr. | Retention time (min) | m/z | Name | GCMS (ppm ±5) | Standard retention time (min) | Standard (ppm ±5) |
|--------------|----------------------|--|---|---------------|-------------------------------|-------------------|
| 1 | 3.4-3.6 | 15; 28; 29; 43; 44 | Acetaldehyde | 11 | 3.4-3.6 | 9 |
| 2 | 3.6-3.7 | 29; 31; 43; 45; 58; 59; 60 | Acetic acid | 31 | 4.4-4.5 | 32 |
| 3 | 5.1-5.3 | 27-29; 31; 37-42; 68-70 | (2,5 or 2,3)- Dihydrofuran | 33 | 5.1-5.3 | 35 |
| 4 | 6.5-6.8 | 28; 31; 42; 47; 59; 72; 74; 86 | Dihydrofuran-2(3 <i>H</i>)- one | 17 | 6.5-6.8 | 18 |
| 5 | 7.0-7.1 | 31; 42; 47; 59; 72; 84 | Furan-2(5 <i>H</i> or 3 <i>H</i>)- one | 21 | 7.0-7.1 | 19 |
| 6 | 9.7-10.0 | 15; 29; 41; 42; 57; 58; 71 | Butyraldehyde | 8 | 9.7-10.0 | 8 |
| 7 | 10.0-10.2 | 15; 18; 19; 25-27; 29; 30; 31; 37; 39; 40-43; 45- 47; 57-60 ; 68-72; 75; 88 | 4-Hydroxybutanal or Tetrahydrofuran-2-ol | 71 | 10.0-10.2 | 69 |
| 8 | 11.7-11.9 | 28; 42; 55; 87 | Succinaldehyde | 22 | 11.7-11.9 | 23 |
| 9 | 12.5-12.8 | 15; 28; 43; 59 | Acetamide | 16 | 12.5-12.8 | 14 |
| 10 | 2.2-2.5 | 16; 17; 18 | Water | 135 | 2.2-2.5 | 138 |
| Total | | | | 354 | | 356 |

*No chlorinated compounds have been detected, which could be associated to transformations of perchlorate anion in the electrolyte.

Table S2. The results for quantification of decomposition products after LiMEAS at 0.8 % O₂ in THF-based electrolyte. The main product is highlighted in bold.

| Nr. | Retention time (min) | m/z | Name | GCMS (ppm ±5) | Standard retention time (min) | Standard (ppm ±5) |
|--------------|----------------------|---|--|---------------|-------------------------------|-------------------|
| 1 | 3.4-3.6 | 15; 28; 29; 43; 44 | Acetaldehyde | 16 | 3.4-3.6 | 14 |
| 2 | 3.8-3.9 | 29; 31; 43; 45; 58; 59; 60 | Acetic acid | 28 | 4.4-4.5 | 27 |
| 3 | 5.1-5.3 | 27-29; 31; 37-42; 68-70 | (2,5 or 2,3)-Dihydrofuran | 45 | 5.1-5.3 | 24 |
| 4 | 10.0-10.2 | 15; 19; 25-27; 29; 30; 31; 37; 39; 40-43; 45-47; 57-60; 68-72; 75; 88 | 4-Hydroxybutanal or Tetrahydrofuran-2-ol | 42 | 10.0-10.2 | 64 |
| 5 | 2.2-2.5 | 16; 17; 18 | Water | 152 | 2.2-2.5 | 155 |
| Total | | | | 283 | | 289 |

*No chlorinated compounds have been detected, which could be associated to transformations of perchlorate anion in the electrolyte.

Table S3. The results for quantification of decomposition products in THF-based electrolyte after LiMEAS at 3.0 % O₂. The main product is highlighted in bold.

| Nr. | Retention time (min) | m/z | Name | GCMS (ppm ±5) | Standard retention time (min) | Standard (ppm ±5) |
|-----|----------------------|--------------------|--------------|---------------|-------------------------------|-------------------|
| 1 | 3.4-3.6 | 15; 28; 29; 43; 44 | Acetaldehyde | 6 | 3.4-3.6 | 8 |

| | | | | | | |
|--------------|------------------|--|---|------------|------------------|------------|
| 2 | 3.8-3.9 | 29; 31; 43; 45; 58; 59; 60 | Acetic acid | 48 | 4.4-4.5 | 47 |
| 3 | 5.1-5.3 | 27-29; 31; 37-42; 68-70 | (2,5 or 2,3)- Dihydrofuran | 39 | 5.1-5.3 | 41 |
| 4 | 10.0-10.2 | 15; 19; 25-27; 29; 30; 31; 37; 39; 40- 43;45-47;57-60 ; 68-72; 75; 88 | 4-Hydroxybutanal or Tetrahydrofuran-2-ol | 25 | 10.0-10.2 | 24 |
| 5 | 2.2-2.5 | 16; 17; 18 | Water | 215 | 2.2-2.5 | 230 |
| Total | | | | 333 | | 350 |

*No chlorinated compounds have been detected, which could be associated to transformations of perchlorate anion in the electrolyte.

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