Supporting information

A lactic acid dioxolane as a bio-based solvent for lithium-ion batteries: physicochemical and electrochemical investigations of lithium imide-based electrolytes

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Table S1. Relevant parameters for LA-H,H and benchmark EC, DMC and EC/DMC (1:1 vol) solvents.

Parameter	EC	DMC	EC:DMC	LA-H,H
Density [g mL^{-1}]	1.32 at 40 °C [1]	1.07 at 25 °C[2]	1.21 at 20 °C[3]	1.12 at 20 °C*
Volumetric expansion [$°C^{-1}$]	0.0007[4]	0.0013[5]	0.0012[3]	0.0010*
Viscosity [mPa s]	1.9 at 40 °C[6]	0.585 at 25 °C[7]	1.68 at 20 °C [8]	1.73 at 20 °C*
Vapor pressure [mmHg]	0.16 at 20 °C[1]	18 at 21.1°C[2]	n.d.	1.7 at 25 °C[9]
Boiling point [°C]	248[1]	90[2]	n.d.	161 – 164[10]
Melting point [°C]	36[1]	2-4[2]	7.9[11]	< -70[10]
Flash point [°C]	143[1]	16[2]	24 [8]	60*
Dielectric constant	89.8[12]	3.1[12]	23[13]	n.d.
Hazardous potential[#]	High[14]	Low[14]	High[14]	Low [10]

* This work

[#] Hazardous potential specifics: **EC**, this substance is harmful if swallowed, causes serious eye irritation and may cause damage to organs through prolonged or repeated exposure; **DMC**, this substance is a highly flammable liquid and vapour. **EC:DMC**, as mixture, it was reported in the table with a label of the more hazardous component. **LA-H,H**, this substance is not regestired by the European Chemical Agency (REACH regulation), its computational struture-response investigation indicate that this substance might be non-carcinogenic and non-reprotoxic

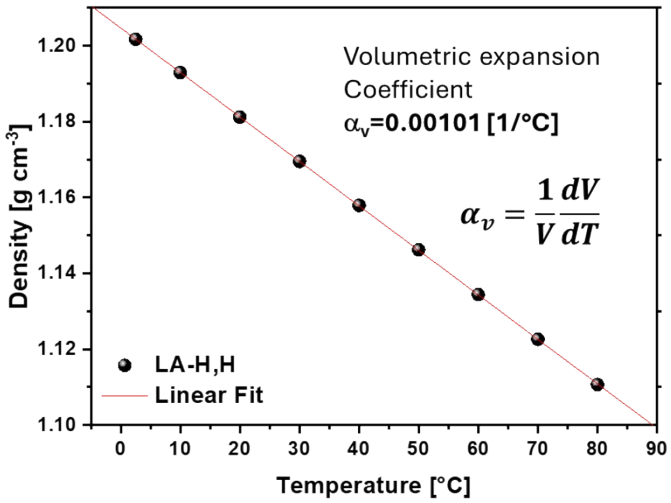

Fig. S1. LA-H,H solvent density over 0-80 °C temperature range.

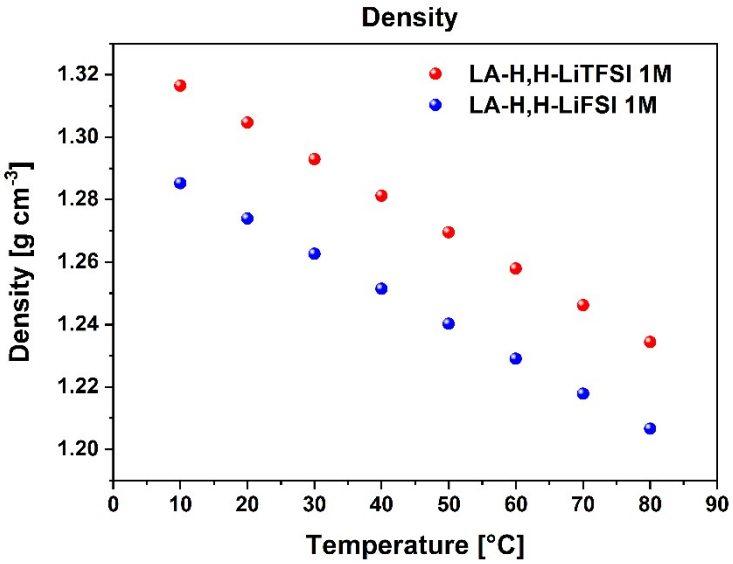

Fig. S2. Electrolyte density measured over 10-80 °C temperature range.

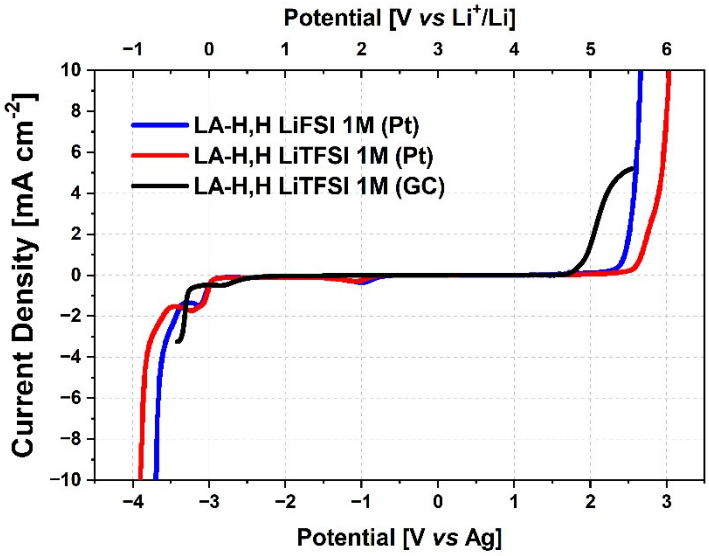

Fig. S3. Electrochemical stability window. Cell set-up: WE, Pt or GC disc; *quasi*-RE Ag; CE, self-standing active carbon electrode. Potential *vs* Li^+/Li was estimated considering the Li *vs* Ag potential (+3.05 V).

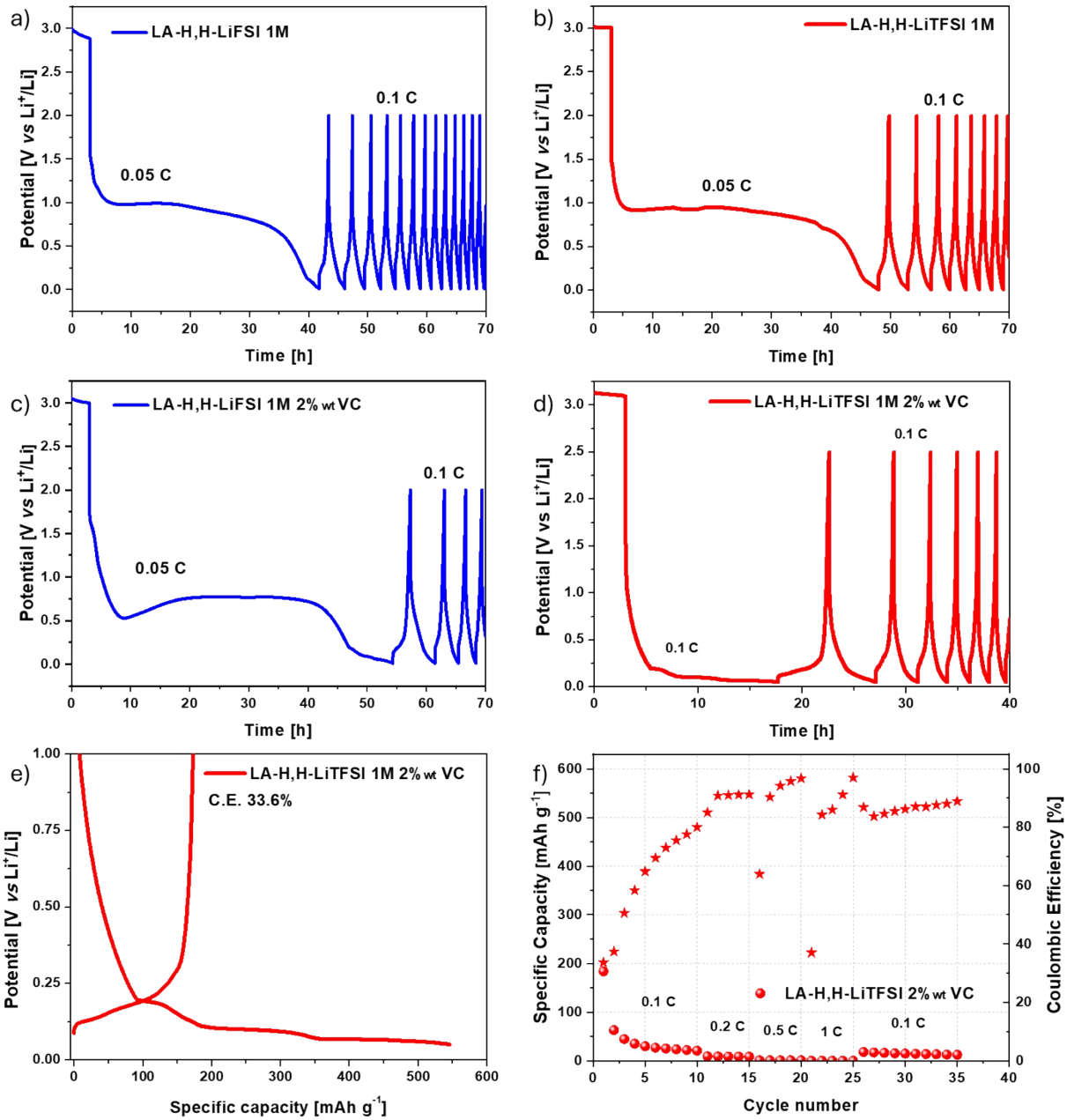

Fig. S4. Example of potential profile of a) LA-H,H-LiFSI 1M and b) LA-H,H LiTFSI over cycling at 0.05 C and 0.1 C without additive, and c,d) with 2%$_{wt}$ of VC with GR. e) First cycle at 0.1 C of LA-H,H-LiTFSI 1M 2%$_{wt}$ VC, and f) C-rate performance over cycling. C.E.: Coulombic Efficiency.

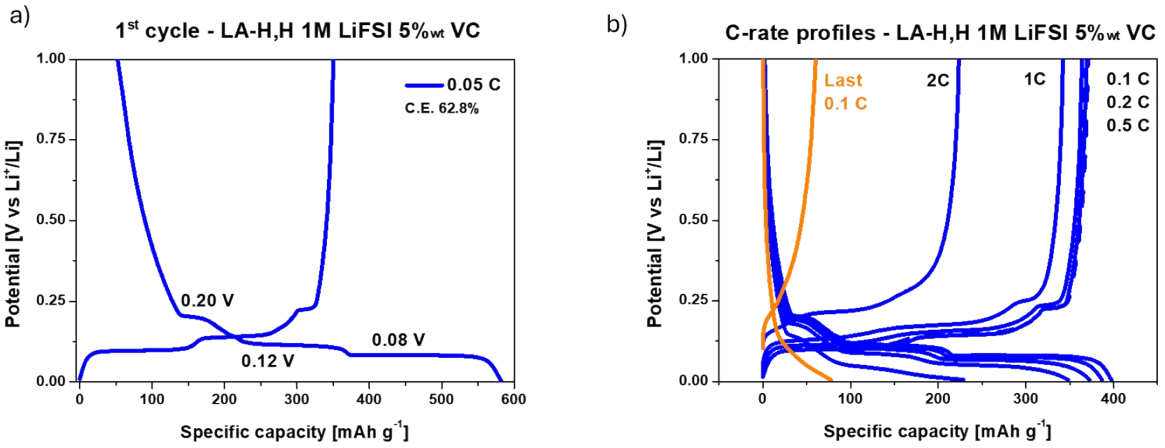

Fig. S5. Galvanostatic charge/discharge profile with LAHH-LiFSI 1M VC 5%$_{wt}$ of a) 1st cycle at 0.05 C, and b) profiles at different current densities over capability test with GR. C.E.: Coulombic Efficiency.

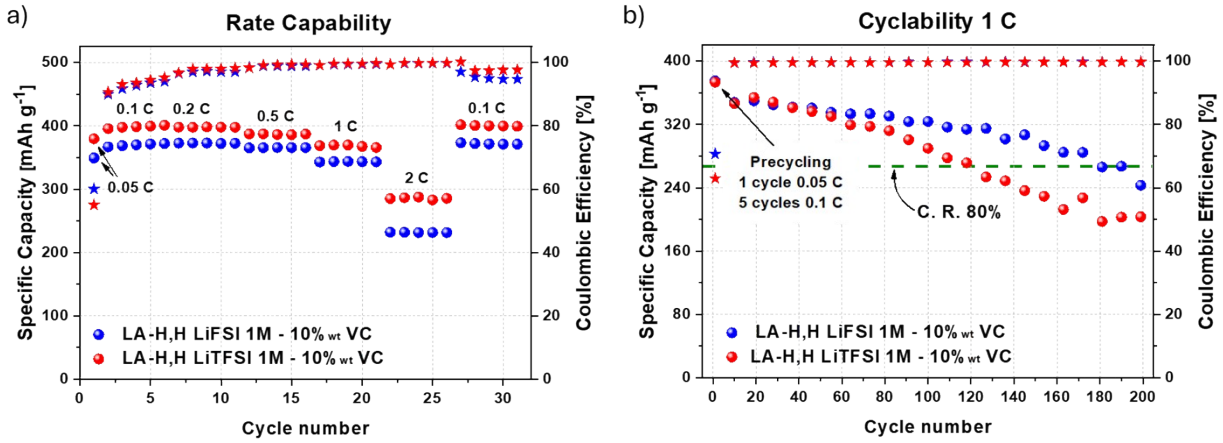

Fig. S6. a) Rate capability and b) cyclability of LA-H,H imide-electrolytes with 10 %$_{wt}$ of VC with graphite electrodes. C.R.: Capacity Retention.

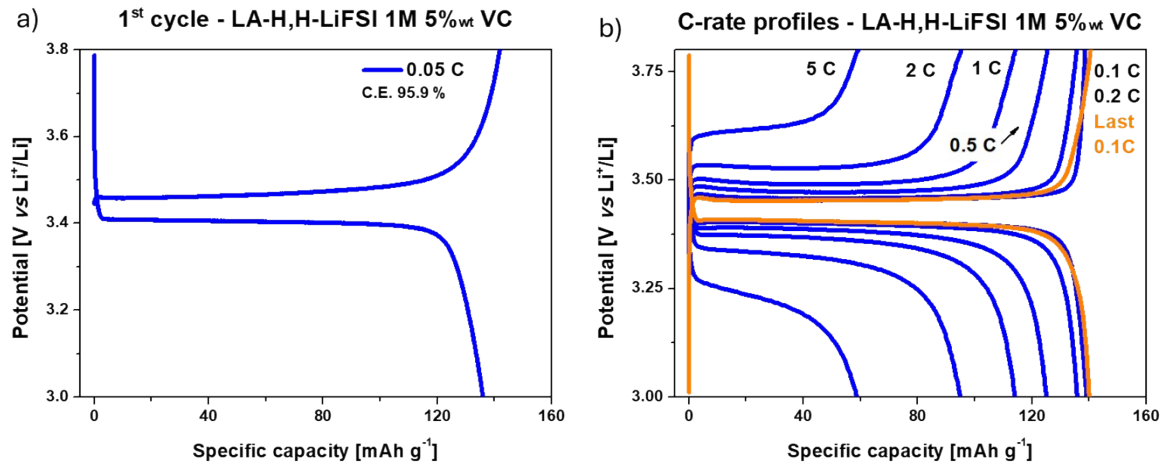

Fig. S7. LFP galvanostatic charge/discharge profile with LA-H,H-LiFSI 1M VC 5%$_{wt}$ of a) 1st cycle at 0.05 C, and b) profiles at different current densities over capability test. C.E.: Coulombic Efficiency.

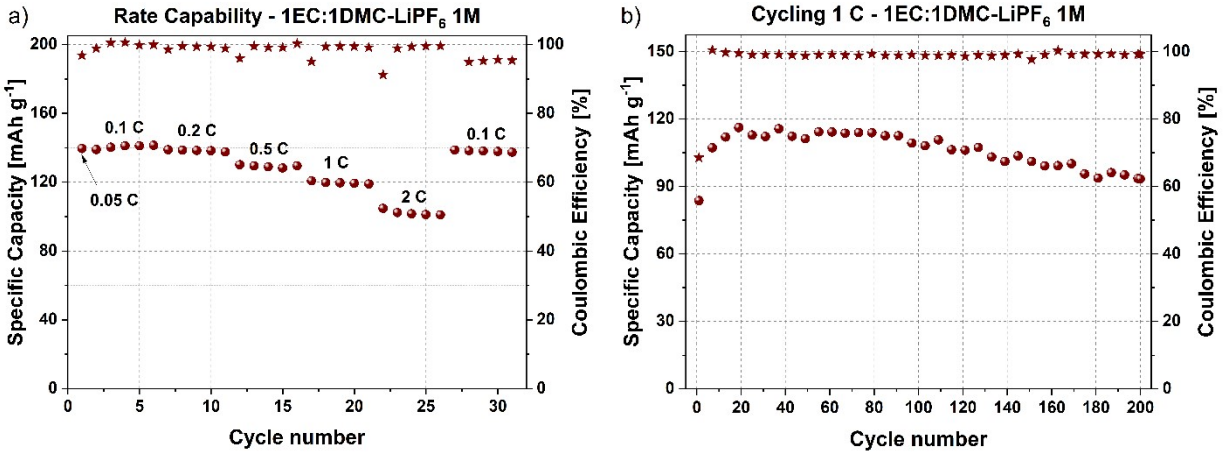

Fig. S8. a) Rate capability and b) cyclability of 1EC:1DMC-LiPF$_6$ 1M electrolyte (LP30) with LFP electrodes.

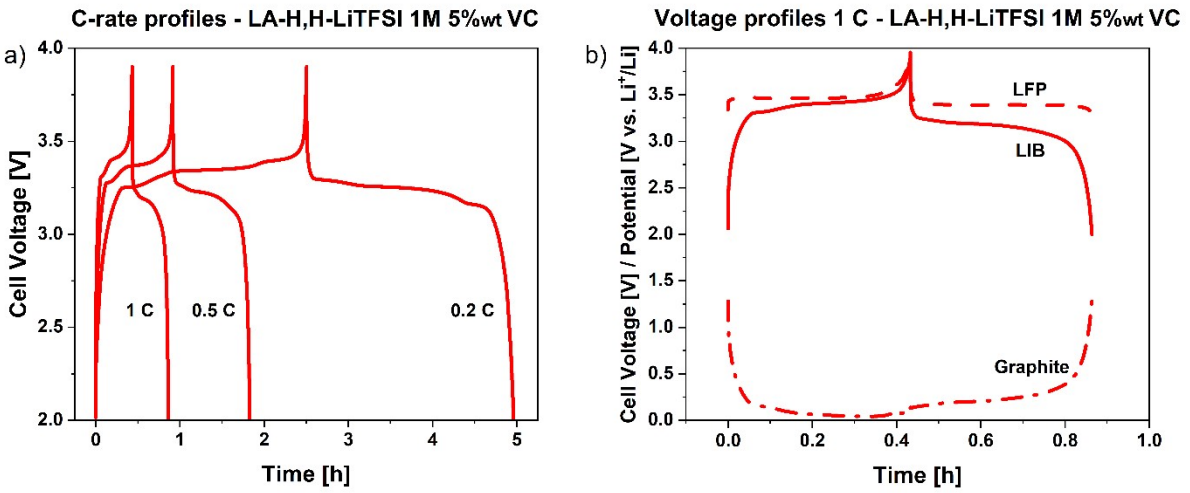

Fig. S9. LFP/graphite LIB full-cell a) galvanostatic charge/discharge profiles with LA-H,H-LiTFSI 1M VC 5%wt for noted current densities, and b) profiles of the full-cell, LFP and graphite electrode at 1 C.

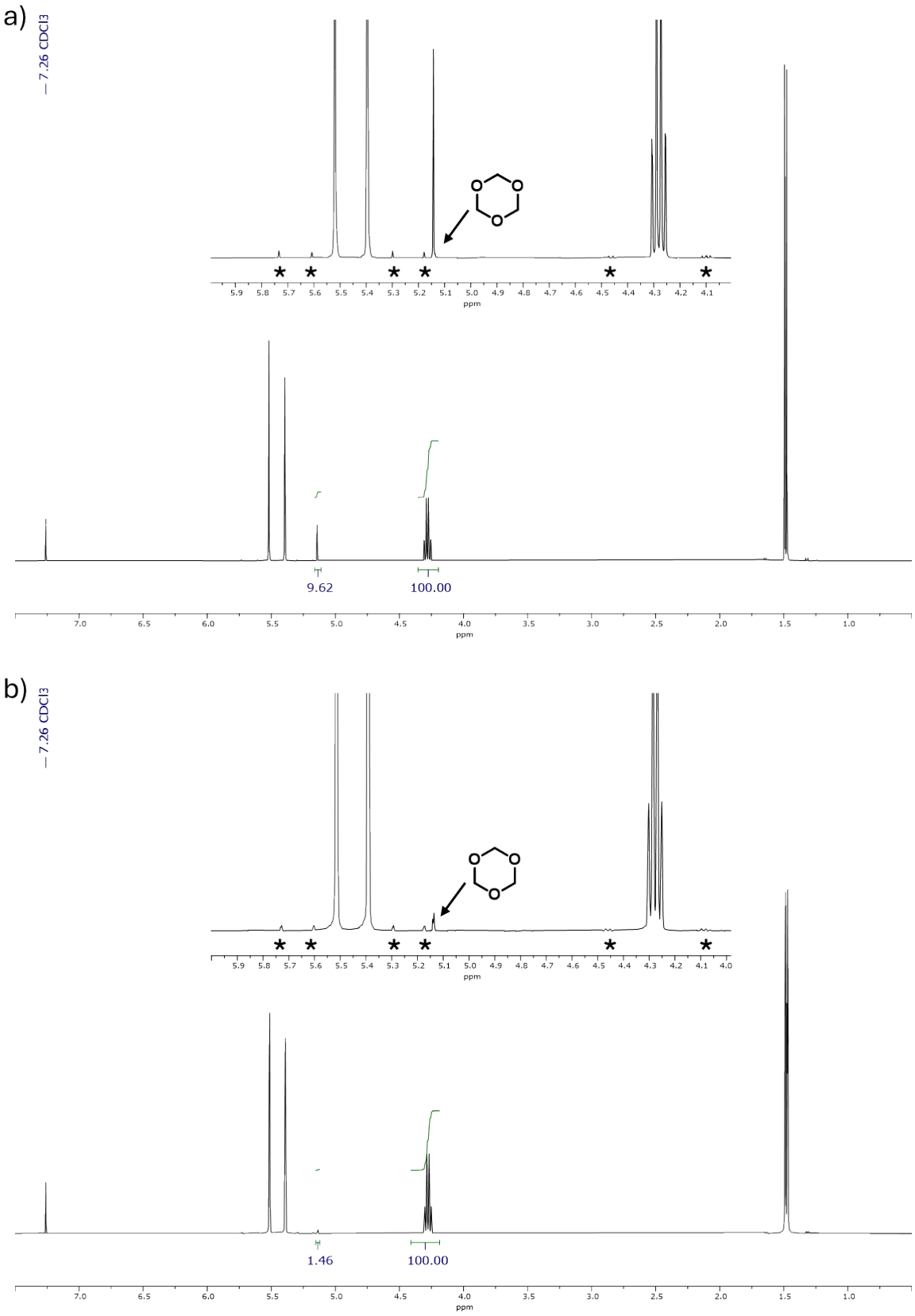

Fig. S10. Relevant 1H NMR spectra (80-100 mg in 0.5 mL CDCl3) of LA-H,H distillation: a) "head", and b) core fractions. Asterisks (*) are used to highlight ^{13}C coupling. LA-H,H purity is evaluated by the ratio of the normalized integrals. In spectrum a) the purity was assessed < 99 % (98.4 %), while in spectrum b) it was assessed > 99 % (99.7 %).

Paragraph S1. NMR analysis details.

Solvent batches with impurities > 1% have been discarded or redistilled until > 99 % is achieved. Typically, discarding the first distillation portion (3-5 mL) from the head fraction is enough to ensure the target purity in the core fraction. The main impurity found during the investigation was identified as trioxane at 5.13-5.14 ppm. Other identified side products from the crude reaction mixture are lactate oligomers, which remain in the distillation tail, and paraformaldehyde oligomers residues, which degrade during the vacuum-distillation process. Formaldehyde contaminants, if present, can be found at 9.7 ppm, and at 4.7-4.6 ppm in its hydrated form (e.g. ($HO(CH_2O)_2H$) and ($CH_2(OH)_2$))[15].

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