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Long-term continuous ammonia electrosynthesis

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Ammonia is crucial in fertilizer and chemical industries and is seen as a carbon-free fuel[1]. The ammonia electrosynthesis from nitrogen at ambient conditions offers an attractive alternative to the Haber-Bosch process[2,3]. The lithium-mediated nitrogen reduction (Li-NRR) represents a promising approach for continuous-flow ammonia electrosynthesis, coupling nitrogen reduction with hydrogen oxidation[4]. However, tetrahydrofuran (THF), commonly used as a solvent, impedes long-term ammonia production due to polymerization and volatility issues. Here we show that a chain ether-based electrolyte enables long-term continuous ammonia synthesis. We find that a chain ether-based solvent exhibits non-polymerization properties, a high boiling point (162 °C), and forms a compact solid-electrolyte interphase (SEI) layer on the gas diffusion electrode (GDE), facilitating ammonia release in the gas phase and ensuring electrolyte stability. We demonstrate 300 hours continuous operation in a flow electrolyzer with 25 cm^2 electrode at 1 bar and room temperature, and achieve a current-to-ammonia efficiency of 64 ± 1% with unprecedented gas phase ammonia content of ~98%. Our work highlights the crucial role of the solvent in long-term continuous ammonia synthesis.

The Li-NRR in non-aqueous electrolytes was first reported in 1930 by Fichter *et al.*[5] using an alcohol solvent with lithium chloride at 1000 bar N_2 and was investigated by Tsuneto *et al.*[6,7] in 1993 using a ring ether-based solvent (i.e., THF) with lithium perchlorate. Since our group first validated that nitrogen molecules are indeed activated in the Li-NRR process to produce ammonia through a rigorous procedure[8], different strategies have been reported to improve the ammonia faradaic efficiency (FE)[9-11], current density[12,13], and stability[14]. Nevertheless, most Li-NRR investigations have been conducted using batch reactors, which present challenges due to the use of sacrificial solvents as proton donors and difficulties in scaling up production.

A promising strategy to establish a sustainable hydrogen source for ammonia synthesis involves incorporating a hydrogen oxidation reaction (HOR) on the anode[4,11,15]. Lazouski et al. first proposed using a stainless-steel cloth (SSC) as the GDE for Li-NRR and using Pt-coated SSC for HOR in a three-compartment cell[15]. Our recent work highlights the use of a PtAu alloy catalyst for HOR in organic electrolytes[4], and demonstrates a 10-hour continuous operation that achieved ammonia FE of 61%. Nonetheless, all previous reports have been unable to achieve long-term continuous-flow ammonia electrosynthesis beyond 10 hours and to demonstrate ammonia production at a gram scale (Fig. 1a). One of the main reasons is the polymerization and volatility of THF[6, 8-19] (Fig. 1b). Further, severe solvent oxidation phenomena were observed due to the use of a sacrificial agent[16]. In a continuous-flow reactor, the Li^+ is reduced on the cathode to form metallic Li and then reacts with N_2, followed by protonation and subsequent production of ammonia (Fig. 1c). The proton is generated from HOR on the anode and delivered by a proton shuttle, e.g., ethanol (EtOH). However, the ring-opening polymerization[20] and low boiling point of 66 °C of THF impedes the long-term continuous-flow operation. Therefore, new solvents are highly desirable for the long-term continuous ammonia synthesis (Fig. 1c): (I) The solvent should enable noticeable solubility of the lithium salt, ensuring high ionic conductivity and facilitating lithium plating. (II) The solvent must be compatible with metallic lithium to form a suitable SEI layer, while also being compatible with a proton shuttle to facilitate the delivery of protons generated from the HOR. (III) The presence of ammonia in the gas phase is highly desirable, which allows for easier and more cost-effective separation. To achieve this, the solvent-induced SEI on the GDE needs to be compact without obstructing the release of ammonia into the gas phase. (IV) To enhance long-term stability, the solvent must possess both non-polymerization capabilities to prevent electrolyte degradation and a high boiling point to avoid electrolyte evaporation.

Solvent effects for Li-NRR

To assess the capability of different ether-based solvents for Li-NRR, especially two kinds of ring ether-based solvents (THF and 1, 3-dioxolane, named DOL) and two kinds of chain ether-based solvents (dimethoxyethane, named DME, and diethylene glycol dimethyl ether, named DG), all experiments were performed using a continuous-flow reactor with a 25 cm^2 effective area GDE, as described in Methods section and Supplementary Fig. 1. It should be pointed out that although DG has been reported for Li-NRR with different lithium salt (i.e., lithium triflate) by our group[21], the micro-chip-based cell for electrochemistry mass spectrometry set-up is far away from the continuous-flow reactor. Our previous study has showcased a potential cycling strategy[4,14] (1 min for Li deposition following by 1 min resting at open circuit voltage, defined as cycling in this work) that can improve the performance of Li-NRR using THF. However, we found that controlling the resting potential (defined as controlled cycling) rather than the resting time is critical for the improved performance using DME and DG, because the ending potential above the Li deposition potential directly indicates the consumption of metallic lithium or lithium nitride species (Supplementary Fig. 2-9).

Li-NRR coupled with HOR in the continuous-flow reactor with controlled cycling leads to the average anode potential staying around 0.6 V versus Pt, and a total cell voltage of 4.0 V for DG (Fig. 2a). Compared with THF, DME and DG exhibit the lower electrolyte resistance (Supplementary Fig. 10). The promotional effect of controlled cycling is observed for both DME and DG (Fig. 2b, Supplementary Fig. 2-7). At the optimal EtOH concentration with controlled cycling, a FE of 81 ± 1% and 76 ± 1% was achieved using DME and DG, respectively, which are higher than that of THF (63 ± 1% FE). In the case of THF with cycling, a relatively low amount of metallic Li might be plated when applying potential, allowing it to be fully utilized for nitridation and protonation within 1 minute of open circuit voltage (OCV). This essentially achieves a comparable efficiency to controlled cycling. Moreover, more than 60% of produced ammonia is distributed in the gas phase using DG with controlled cycling (Fig. 2c, Supplementary Table 1). Compared with controlled cycling, the non-controlled cycling could potentially lead to a relatively thicker SEI layer and further induce the ammonia trapped in the electrolyte. The compatibility of DME and DG with EtOH were also proved by D_2 isotype studies in the continuous-flow reactor (Supplementary Fig. 11, 12). An operando mass spectrometry experiment of 28 hours was further carried out using DG for monitoring the on-site hydrogen and ammonia production in the gas phase (Fig. 2d). After first switching from OCV to the lithium deposition potential, ammonia starts to be formed and produced continuously over the duration.

Stability of electrolyte

Regarding the capability of DOL for Li-NRR, the initially liquid $LiBF_4$-DOL electrolyte transitions into a gel-state electrolyte after 2 hours, even without electrochemistry (Fig. 3a). New hydrogen peaks in accordance with the structure of polyDOL are also observed in the nuclear magnetic resonance (NMR) analysis[22,23]. The $LiBF_4$-THF electrolyte is also transformed to a gel-state electrolyte (Fig. 3b) after a 14-hour Li-NRR operation in the continuous-flow reactor due to the THF polymerization[24,25]. It has been reported that the breaking of the C-O bond is the cause of the THF polymerization[26]. Based on extended *ab initio* molecular dynamics (AIMD) simulations of THF with and without dissolved lithium salt, we have provided additional evidence for this picture. We show that the C-O radial distribution function exhibits a stretched C-O bond in the presence of lithium salt (Supplementary Fig. 13, 14), indicating a weakened C-O bond and hence more facile C-O bond breaking.

For the $LiBF_4$-DG electrolyte, on the other hand, no visible change can be observed over 300-hour continuous Li-NRR operation (Fig. 3c). The electrochemical oxidation of THF, DME, and DG in an aqueous electrolyte also indicates the superior stability of DG and DME (Supplementary Fig. 15)[27-29]. These findings emphasize the stability of DG as an efficient solvent in practical Li-NRR process. More detailed investigations of the long-term continuous Li-NRR operation are discussed in the following section.

X-ray photoelectron spectrometer (XPS), X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to investigate the key role of the solvent in the SEI formation (Supplementary Fig. 16-18). The deposited layer using DG shows particle-like deposits, appearing thin and uniform, while the deposited layer using THF not only covered the GDE but also was interconnected and blocked its pores (Fig. 3d, e, Supplementary Fig. 19-21). Cryogenic transmission electron microscopy (cryo-TEM) images further confirmed the presence of nanoparticles with a mean size of 13 ± 2 nm in the deposited layer using DG (Supplementary Fig. 20). After 100 and 300 hours of operation, increased particle-like deposits covered the electrodes, with nanoparticles sizes growing to 16 ± 3 and 22 ± 3 nm, respectively. The deposited layer reached a thickness of ~240 nm after 300 hours (Supplementary Fig. 21), forming a compact SEI mainly composed of nanoparticles ranging from 13-22 nm over 300 hours. Contrary to these results, the deposit on the GDE using THF comprised of particles averaging 433 ± 78 nm in size after only

2.4 hours (Supplementary Fig. 22). High resolution cryo-TEM (HR-TEM) images revealed a complex structure of the SEI layer using DG (Supplementary Fig. 23), featuring nanoscale regions of crystalline species. Selected area electron diffraction (SAED), HR-TEM, and SEM with energy dispersive x-ray spectroscopy also implied that these regions consist of LiF (Supplementary Fig. 23, 24). Further, the main inorganic component of LiF in the different deposit layers is confirmed by XRD and depth-profiling XPS (Supplementary Fig. 25-30).

Considering the trace amount of water that is typically present in the fresh electrolyte, the effect of H_2O concentration is also investigated (Fig. 4, Supplementary Fig. 31-33). The electrochemical performance and FE do not exhibit obvious changes as the H_2O concentration increased from 1.6 to 16.1 mM with optimal EtOH concentration (25.8 mM) in DG (Fig. 4a, Supplementary Fig. 31), which indicates a certain amount of H_2O tolerance (1.6 to 16.2 mM) in the system. However, the FE and stability notably decline with H_2O concentrations surpassing 20.9 mM (Fig. 4a, Supplementary Fig. 32). Specifically, the resting time for the cathode potential to return to -2.5 V intensively increased, accompanied by a dramatic FE drop to 7 ± 1%. This is potentially caused by a passivated SEI layer due to excessive H_2O content, which blocked the consumption of metallic lithium. The phenomenon regarding increased resting time is more notable as the H_2O concentration further increased to ~31.6 mM. Moreover, without the presence of EtOH, less ammonia produced and most of the ammonia is present in the electrolyte rather than in the gas phase (Fig. 4b). It indicates that water alone, without EtOH, cannot sustain the long-term continuous ammonia electrosynthesis.

Long-term operation

The long-term stability in a continuous-flow reactor was evaluated with controlled cycling (Supplementary Fig. 34-39, Table 2-7). The anode potential started to increase after 10 hours with THF, and kept increasing to 1.68 V after 14.4 hours until we manually terminated the reaction due to severe THF evaporation and polymerization (Fig. 5a). DME provides better stability but also exhibits a similar anode potential increase after 26 hours, and electrolyte loss due to DME evaporation (boiling point of 85 °C). On the contrary, four independent 300-hour continuous operations were enabled by using DG (Fig. 5b), and the average anode potential is less than 1 V over the whole duration. The accelerated passed charge over time is ascribed to the reduced time at resting periods, likely linked to SEI buildup and stabilization. Electrolyte water content, pH, and

temperature may also affect SEI buildup and stabilization. An ammonia FE of 64% was achieved using DG after 300-hour operation with a slight degradation towards the end (Fig. 5c), while THF obtained 28% FE after 14 hours and DME obtained 48% FE after 27 hours. The severe ammonia FE decay using THF is due to electrolyte degradation from THF evaporation, polymerization, and high anode potential leading to THF oxidation. After 300-hour operation, 3 mL DG had evaporated from 120 mL electrolyte, while 90 mL THF had evaporated only after 14 hours. In addition, 5% EtOH was consumed, and no obvious Li and B consumption was observed over 300-hour operation (Supplementary Fig. 40-42). Pre-saturating the N_2 and H_2 with solvent could mitigate solvent loss in long-term experiments, and is worth considering for scale-up.

The ammonia distribution in the gas phase and electrolyte is found to be strongly dependent on the type of solvent used (Fig. 5d, Supplementary Fig. 43). Specifically, ~98% of ammonia accumulated in the gas phase for DG after 300 hours. The ammonia concentration in the electrolyte did not reach a point of saturation but more ammonia began distributing in the gas phase (Supplementary Fig. 44), possibly due to an ammonia concentration gradient in the electrolyte. We obtained more than 4.6 g of ammonia in total after 300 hours, and 4.5 g of ammonia in the gas phase. This marks the first Li-NRR demonstration for ammonia production at a gram scale, with over 95% of the produced ammonia observed in the gas phase, a novel achievement. Stability, FEs, and energy efficiencies (EEs) of previous publications are summarized in Fig. 5e and Supplementary Table 8 for comparison. We achieved 17% EE and 300 hours stability using DG, both are highest among all the reported results. Notably, theoretical maximal EE for Li-NRR process is ~28% based on our previous calculation[4]. Notably, reported EEs in continuous-flow reactors include H_2 as the proton source, whereas pseudo-EEs in batch reactors exclude the energy for H_2 synthesis, without demonstration of proton origin from hydrogen or sacrificial agents.

The findings presented here mark progress in identifying stable solvents for achieving long-term stability and optimal product distribution in continuous-flow ammonia electrosynthesis via Li-NRR. We also demonstrate the feasibility of using high surface area GDE in the continuous-flow reactor to increase the current density from -6 to -60 mA cm^{-2} (Supplementary Fig. 45). While significant, this doesn't address all Li-NRR challenges for industrial application. Achieving industrial relevant current densities demands optimizing GDE, electrolyte formulation, cycling procedure, and reactor design. Future Li-NRR research should target high FE and EE at industrial

relevant current densities while maintaining long-term stability and gas-phase ammonia in pilot-scale flow cells.

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Figure legends

Fig. 1 Schematic illustration for long-term electrochemical ammonia synthesis. a, Produced ammonia versus stability reported in batch reactors (blue and purple squares)[8-13,17,18], continuous-flow reactors (orange circle)[4,15], and this work (red circle). **b**, Overview of solvent developed for lithium-mediated ammonia synthesis. **c**, Comparison of long-term continuous ammonia synthesis with different solvents. The solvent greatly affects the electrolyte stability and the derived deposit including the SEI on the gas diffusion electrode, as well as the ammonia distribution in the gas phase.

Fig.2 Investigation of different solvents in a continuous-flow reactor. a, Chronopotentiometry at the current density of -6 mA cm^{-2} with DG and EtOH concentration of 43.0 mM. All reported potentials are presented without ohmic drop correction. **b**, The effect of EtOH concentration, controlled cycling, and solvent on the ammonia FE. **c**, The effect of controlled cycling and solvent on the ammonia distribution in the electrolyte, gas phase, and electrode deposits at the EtOH concentration of 43.0 mM. **d**, Operando mass spectrometry of the cathodic gas products over 28 hours. The upper panel is the applied potentials during the controlled cycling at the current density of -6 mA cm^{-2}. The bottom panel is the measured ammonia and hydrogen products. Error bars show the standard deviation from at least three independent experiments.

Fig. 3 Structure analysis of the solvent and gas diffusion electrode for the continuous ammonia electrosynthesis. a, Hydrogen NMR spectra of the DOL-based electrolyte before and after 2 hours of rest. **b**, **c**, Hydrogen NMR spectra of the THF-based electrolyte after 14 hours (**b**) and diglyme-based electrolyte after 300 hours (**c**). Insets in (**a**) and (**b**) are the corresponding digital

photographs of the liquid electrolyte before and after the reaction. Insets in (**c**) are the corresponding digital photographs of the liquid electrolyte during the reaction. **d**, **e**, Representative SEM images of the gas diffusion electrode after using THF-based (**d**) and DG-based (**e**) electrolyte for continuous ammonia electrosynthesis with the same passed charge of 700 C.

Fig. 4 The effect of water concentration. a, **b**, The effect of water concentration on the ammonia FE (**a**) and ammonia distribution in the electrolyte, gas phase, and electrode deposits (**b**). With or no EtOH shown in (**a**) and (**b**) means electrolyte with optimal EtOH concentration of 25.8 mM or without EtOH. Error bars show the standard deviation from at least three independent experiments.

Fig. 5 Long-term ammonia electrosynthesis in continuous-flow reactor. a, **b**, Long-term ammonia synthesis with controlled potential cycling at -6 mA cm^{-2} using THF, DME (**a**), and DG. (**b**). **c**, **d**, The evolution of the ammonia FE (**c**) and ammonia distribution in gas phase and electrolyte (**d**) over passed charge for the long-term experiments using different solvents. **e**, Comparison of the stability, FE and EE with literature results using batch reactor with THF (purple boxes)[8-15,17,18], continuous-flow reactor with THF (brown cylinder)[4,15] and DG (red cylinder, this work).

Methods

Preparation of electrodes

The 36 cm^2 316 stainless-steel cloth (SSC, McMaster-Carr, 500 × 500 mesh, pore size: 30 μm) was used as the working electrode (WE). The PtAu catalyst electrodeposited on the same type of SSC electrode (PtAu/SSC) was prepared by the hydrogen bubble method. Prior to use, the SSC was washed with acetone and ethanol three times. To achieve uniform PtAu electrodeposition, the two Pt meshes (Goodfellow, 1.5 cm×1.5 cm, 99.9 %) were electrically connected and used as a split counter electrode, where the working electrode (SSC) was placed in the middle between counter electrodes. The 10 mM $H_2PtCl_6 \cdot 6H_2O$ (Sigma Aldrich, ACS reagent) with 10 mM $HAuCl_4 \cdot 3H_2O$ (Sigma Aldrich, 99%) in 3 M H_2SO_4 (Sigma Aldrich, 99.999%) solution was used as an electrolyte for electrodeposition PtAu/SSC. A current density of -0.2 A cm^{-2} was applied for 2 min, leading to high surface area structures of PtAu on the SSC. The 0.4 M $CuSO_4$ (Merck, 98%) in 1.5 M H_2SO_4 (Sigma Aldrich, 99.999%) solution was used as an electrolyte for electrodeposition Cu/SSC. A current density of -1.0 A cm^{-2} was applied for 1 min, leading to high surface area structures of Cu on the SSC. After the electrodeposition, the electrodes were rinsed in EtOH and ultra-pure water (18.2 MΩ resistivity, Millipore, Synergy UV system) several times to remove all residual electrolytes.

Electrochemical experiments in a continuous-flow reactor

Electrochemical ammonia synthesis was conducted in a three-chamber flow cell (Supplementary Fig. 1). The dimension of the flow cell was 10.7 cm×10.7 cm×5.1 cm. The effective area of the flow field was 25 cm^2. The size of gas flow channels was 1 mm. The thickness of the central electrolyte chamber is 4 mm. The SSC (500 × 500 mesh, pore size: 30 μm) was used as WE. As-prepared PtAu/SSC was used as the counter electrode (CE). The pseudo reference electrode (RE) was a Pt wire (Goodfellow, 99.99 %, diameter: 0.5 mm). Before electrochemical tests, the Pt wire was flame annealed. The N_2 (5.0, Air Liquide) and H_2 (5.0, Air Liquide) gas flow rates were controlled using a mass flow controller (Brooks Instrument) and set to 5-75 sccm. The N_2 and H_2 used in the experiments were cleaned by purifiers (NuPure) and all labile N-containing compounds

can be down to parts per trillion by volume (ppt-v) level. The $LiBF_4$ (Sigma Aldrich, ≥ 98%, anhydrous) was dried at 120 ºC for 48 h in a vacuum oven before use. EtOH (Honeywell, anhydrous) was dried with 3 Å molecular sieves. Electrolyte solution consisted of 1 M $LiBF_4$ in solvent (THF, anhydrous, >99.9%, inhibitor-free, Sigma Aldrich, DME or DG, anhydrous, 99.5%, Sigma Aldrich) and 0-172.0 mM EtOH was prepared in an Ar glovebox (Vigor). A peristaltic pump (Baoding Zhunze Precision Pump Manufacturing Co., ltd.) was used to control the flow rate of the electrolytes at 1.0 ml min^{-1} (Supplementary Fig. 46). The electrolyte without any gas pre-saturation was pumped in a loop through the cell and a container. 120 mL electrolyte was used for all the long-term experiments considering the fast evaporation of THF. 60 or 30 mL electrolyte was used for all the short-term experiments. Around 10 sccm N_2 gas is flowed into the container to avoid air exposure of the electrolyte. 75 sccm of N_2 and H_2 gas flow rates were used for all the short-term experiments, and 5 sccm of N_2 and H_2 gas flow rates can be used for the long-term experiments. The pressure gradient (*i.e.* 15 mbar) between the gas inlet and outlet of the flow cell was modulated by a 10.5 centimeters water column (50 mL) above the gas. 10 mM of H_2SO_4 (Sigma Aldrich, 99.999%) or HCl (Sigma Aldrich, Suprapur) solution was used as an NH_3 trap solution. Generally, 1.0-2.6 mM of water content was measured in the as-prepared electrolyte via Karl Fischer Titration (831 KF Coulometer and 728 Stirrer, Metrohm).

Prior to injection of electrolyte into the liquid chamber, the purified N_2 and H_2 (75 sccm) were introduced into the empty assembled flow cell for at least 30 min. Afterward, the electrolyte solution was injected into the cell in N_2 and H_2 atmospheres. The electrochemistry experiments were performed using a BioLogic Potentiostat (VMP2). The resistance between the WE and RE was measured using the potentiostatic electrochemical impedance spectroscopy. The linear sweep voltammetry was recorded from the OCV until lithium reduction is clearly seen. Subsequently, Chronopotentiometry (CP) was measured. In the normal cycling, -6 mA cm^{-2} was applied for 1 min and then 0 mA cm^{-2} for 1 min. In the controlled cycling, -6 mA cm^{-2} was applied for 1 min and then 0 mA cm^{-2} is kept until the cathode potential reached the target potential, e.g., -2.8 to -2.2 V, typically -2.5 V. 297 C of charge was passed for each short-term experiment unless otherwise specified. All experiments were conducted at room temperature and 1 bar. Typically, flow cell experiments were performed in a fume hood. For analysis of the SEI on the working electrode, the flow cell was run in an Ar glovebox. When the experiment was finished, produced NH_3 was distributed in three parts, (1) gas-phase NH_3 trapped in 10 mM of H_2SO_4 or HCl, (2) NH_3 trapped in the electrolyte, and (3) NH_3 trapped in the electrode deposits. Typically, 120 ml of ultra-pure water was used to dissolve the electrode deposits to release trapped NH_3, since H_2O can react with intermediate nitrogen species (*e.g.* Li_3N) in the electrode deposits to produce NH_3. After the short-term experiment, the water content of the electrolyte was increased to 5.2-7.8 mM. The water content of the electrolyte was increased to 13.6 to 14.0 mM after 300 hours experiment.

For the experiment operated at -60 mA cm^{-2} using 25 cm^2 high surface area Cu/SSC, the thickness of the central electrolyte chamber is 1 mm, and the electrolyte solution consisted of 1 M $LiBF_4$ in DG and 172.0 mM EtOH. In the controlled cycling, -60 mA cm^{-2} was applied for 1 s and then 0 mA cm^{-2} is kept until the cathode potential reached -2.5 V. All the other conditions are the same as the experiments operated at -6 mA cm^{-2}. The electrode used for higher current densities is made of highly structured Cu (with particles diameter of 1 to 3 μm) self-assembled on the SSC (Supplementary Fig. 45a, b). Based on our developed kinetic model that describes the mechanism of Li-NRR[14], the H^+, N_2, and Li^+ diffusion rates also need to be rebalanced at high current density to maintain the high ammonia FE. Therefore, the EtOH concentration is increased from 43.0 (at -6 mA cm^{-2}) to 172.0 mM at -60 mA cm^{-2}, and the deposition time in the controlled cycling procedure is decreased from 1 min to 1 s to avoid thick lithium deposits. The anode potential and cell voltage stays stable around 0.7 V (versus Pt) and 4.3 V at -60 mA cm^{-2}, respectively

(Supplementary Fig. 45c-e). Notably, achieving 297 C takes only 29 minutes at -60 mA cm^{-2}, contrasting with 260 minutes at -6 mA cm^{-2}, indicating a comparable ratio of resting and deposition periods at these two current densities. Comparable FE and gas-phase ammonia were achieved at -60 mA cm^{-2} compared with -6 mA cm^{-2} (Supplementary Fig. 45f). The electrolyte formulation, high surface area GDE, and continuous-flow reactor reported in the present work are not the final version for practical or commercial use. However, these results serve as a promising foundation for further enhancements in current density through systematic optimization of the above parameters.

D_2 oxidation experiment via operando mass spectrometry

Mass spectrometry (MS) measurements were collected with a QMG 422, using a 100 mm long QMA 120 quadrupole mass filter (QMS) from Balzers. The QMS was optimized for soft ionization measurements at 26 eV ionization energy, ensuring minimum cracking patterns in the mass spectra, while allowing for a decent signal. The MS is placed downstream on the N_2 flow from the cathode side of the flow cell (Supplementary Fig. 47). This allows for *operando* measurements of the flow cell operation and performance. The connecting gas line is heat traced to 100 °C, to avoid sticking ammonia to the inner tube walls and increase collection efficiency and time resolution. The continuous gas collection is through a 1 μm flow calibrated orifice from Lenox Laser. Measurements with electrolytes in the flow cell are collected under a low vacuum of typically 2.4×10^{-6} mbar, while the vacuum chamber is heated to 120 °C. The vacuum is sustained by a HiPace 300 H Turbo Pump from Pfeiffer Vacuum. The electrochemical reaction was performed as the same condition as the aforementioned continuous-flow reactor. Deuterium (D_2, 99.8 atom% D, 4.5N purity) and nitrogen (N_2, 5N purity) flow rates were controlled with mass flow controllers (Brooks Instrument), and both were set to 50 sccm. D_2 outlet gas was passed directly through a water column, whereas the N_2 gas outlet was flowed by the mass spectrometer before passing through a water column. Once both gases and electrolytes were flowing, the mass spectrometer was started and measured on the N_2 gas outlet. The baseline mass signals were measured starting from the OCV. More details on the calibration curve for mass spectrometry quantification can be found in our previous work[4].

THF, DME, and DG oxidation experiments in aqueous electrolyte

To evaluate the electrochemical stability of THF, DME, and DG on the PtAu anode catalysts, oxidation experiments in an aqueous electrolyte were carried out in a custom-made three-electrode glass cell using the rotating disk electrode method. The Hg/Hg_2SO_4 reference electrode was calibrated before the electrochemistry test and a Pt wire was used as a counter electrode. The working electrode (PtAu/Ti) was obtained from electrodeposited PtAu on a titanium stub (ϕ = 5 mm, 0.196 cm^2). To prepare the PtAu/Ti electrode, an electrolyte of 10 mM $H_2PtCl_6{\cdot}6H_2O$ (Sigma Aldrich, ACS reagent) with 10 mM $HAuCl_4{\cdot}3H_2O$ (Sigma Aldrich, 99%) in 3 M H_2SO_4 (Sigma Aldrich, 99.999%) was used. A current density of -1.0 A cm^{-2} was applied for 2 min in which rigorous hydrogen evolution and metal deposition took place at the same time with 2500 revolutions per minute. The cyclic voltammetry curve was recorded between 0 and 1.4 V vs RHE at 50 mV s^{-1} in Ar-saturated 0.1 M H_2SO_4. THF, DME, and DG oxidation activity were evaluated in Ar-saturated 0.1 M H_2SO_4 with 0.1 M THF or 0.1 M DME or 0.1 M DG electrolyte with a scan rate of 50 mV s^{-1}.

Quantification of ammonia

Produced ammonia was quantified by ion chromatography (IC, Metrohm). The materials of connection tubes, pressure screws, capillaries, and injection needles are PEEK or PTFE (THF-resistant materials). The cation column (Metrosep C6) made by silica gel with carboxyl groups

was used as a high-capacity separation column. The eluent (mobile phase) was 3.3 mM HNO_3 (Sigma Aldrich, Suprapur) solution with 1.35 M acetone (i.e., 10 vol%, Sigma Aldrich, ≥ 99.9%). The eluent flow rate was 0.9 ml min^{-1}. Before use, the eluent was degassed for 30 min to prevent gas bubbles in the high-pressure pump. The sample injection volume was 20 μL. The data acquisition time was 20 min. Ammonium chloride (Sigma Aldrich, 99.998%) solution was used to make the NH_3 calibration curve shown in our previous work[4]. The solution with ammonia was diluted accordingly with ultra-pure water within the range of calibration curve. The sample or diluted sample contains any visible particles was pre-treated by a filter syringe with a PTFE filter membrane (Whatman Puradisc, 0.45 μm) to remove the insoluble substance before testing IC. The ion concentration is proportional to the peak area. All the FE were calculated by the following equation:

$$FE=3\times F\times(c_1\times V_1+c_2\times V_2+c_3\times V_3)/Q \quad (1)$$

where 3 is the number of electrons transferred for each mole of NH_3, F is the Faraday constant, c_1, c_2, c_3 is the concentration of produced ammonia in the electrolyte, gas-phase trapped solution, and electrode deposits dissolved solution, respectively, V_1, V_2, V_3 is the corresponding solution volume, respectively, and Q is the total passed charge. Details on the calculation method for the EEs, including the pseudo-EEs can be found in our previous work[4].

Characterization

XPS (ThermoScientific Thetaprobe), SEM (Quanta FEG 250) and XRD (Malvern Panalytical Empyrean X-ray diffractometer) were used to investigate the SEI on the electrode after electrochemistry. The flow cell experiments were performed in an Ar-filled glovebox (Supplementary Fig. 48) and corresponding transfer system was used to minimize the air exposure of the electrodes (Supplementary Fig. 16-18). All the electrodes were dried after wash treatment (gently dip into the corresponding solvent for 5 times) in the glovebox before characterization, unless otherwise specified. XPS was conducted with an Al Kα x-ray source and base pressure below 9.0×10^{-10} mbar. The ion gun in etching mode and flood gun in charge neutralization mode were used during the measurement with a chamber pressure of 2.0×10^{-7} mbar by flowing Ar gas (99.9999%, Air Liquide). The ion gun was run using 4 kV and 1 μA mode with scanning size of 2×2 mm^2. The spot size of 400 μm were used. All the survey spectra were recorded with step size of 1.0 eV and dwell time of 50 ms at pass energy of 200 eV (Supplementary Fig. 30). High resolution elemental spectra were recorded with step size of 0.1 eV and dwell time of 50 ms at pass energy of 200 eV. All the spectra were acquired and analyzed by Thermo Avantage (v5.9925) by Thermo Fisher Scientific. All the background were determined using Shirley mode and fitted using Powell algorithm. The F 1s spectra of all the electrodes show the two peaks that attributed to LiF and Li_xBF_y[13,19], respectively (Supplementary Fig. 26-29). The ratio of the LiF signal increases as the etching time increases, which indicates a LiF-enriched SEI layer on the GDE. The prominent O 1s C-O peak and C 1s C-C and C-O signals reveal the presence of organic SEI components in all the deposits. The Li 1s and O 1s signal near LiOH binding energy of all the electrodes potentially imply the presence of LiOH. However, no clear crystalline LiOH is observed in cryo-TEM results (Supplementary Fig. 23). Given the complexity of oxygen's chemical states and local probe of cryoEM, further systematic investigations on the different inorganic species are highly recommended. The weak N 1s spectra of electrodes with DG-based electrolyte suggest trace lithium nitride species. The weak signal around 710 eV in Supplementary Fig. 30 is ascribed to the intrinsic shake structure satellites associated with F 1s (main) and the extrinsic scattered electron background[30].

The NMR characterization of the electrolyte samples was performed at 25 °C using a Bruker AVANCE III HD spectrometer operating at ^1H frequency of 800 MHz equipped with a 5 mm TCI

CryoProbe (Bruker Biospin). The chemical shifts were normalized to tetramethylsilane (TMS). The data were analyzed with Bruker Topspin 4.2.0 with an academic license.

After the experiments, the cell was disassembled in the glovebox, and all the dried GDE electrodes after wash treatments can be punched directly into the 3 mm diameter grid in the glovebox (Supplementary Fig. 49), which fits the cryo-TEM holder. All the following steps are consistent with the preparation method shown in the literature using cyro-EM[19]. Specifically, each grid was sealed in an individual Teflon-sealed glass vial and wrapping with parafilm. The vial was then transferred from the glovebox and quickly plunged in liquid nitrogen to freeze. Bolt cutters were used to open the vial and tweezers were used to transfer the grid into a cryo-grid box for storages, all under liquid nitrogen. Then, the cryo-grid box with grid under liquid nitrogen was transferred to a cryo-transfer station, and grid was picked up and affixed to the Gatan 626 cryo-transfer holder. The built-in shutter of the transfer holder remained closed as the sample was inserted into the TEM column around 1 second, ensuring that the sample did not come into contact with the air. The cryo-transfer holder maintains the grid at -175 °C during the imaging. Cryo-TEM was conducted on Tecnai T20 G2, and imaging was done with a TVIPS XF416 CCD camera. Electron flux is less than 10 and 300 e $Å^{-2}$ s^{-1} for low-magnification (SADE) and HR-TEM images, respectively. The electron beam exposure time of each area is less than 10 s with acquisition time of 0.4 to 1 s.

Calculation methods

Density functional theory (DFT) settings: All DFT are performed within the generalized Kohn-Sham scheme[31], using in the Vienna *Ab initio* Simulation Package (VASP)[32], as implemented in Atomic Simulation Environment (ASE)[33]. We use the PBE exchange-correlation functional[34] together with Grimme's D3[35] for dispersion corrections, i.e., PBE-D3. Projector augmented wave (PAW) potentials[36,37] are used with a plane-wave cutoff of 400 eV. Thet spacing between k points[38] is chosen as 0.24 $Å^{-1}$. The Li $1s^2 2s^1$, B $2s^2 2p^1$, O $2s^2 2p^4$, C $2s^2 2p^2$, F $2s^2 2p^5$, and H $1s^2$ electrons are treated explicitly as valence. The electronic energy and structure relaxation were converged within 10^{-7} eV and $\pm 10^{-3}$ eV $Å^{-1}$, respectively.

All AIMD (Born-Oppenheimer) are performed in the *NVT* ensemble at 300 K. The equations of motion were integrated with a time step of 1 fs using the Nosé-Hoover thermostat[39,40]. The 100 ps trajectory after the equilibration of the $LiBF_4$ solvated THF systems is collected for analysis and the 20 ps trajectory after the equilibration of the pure THF solvent system is collected for analysis. All the MD trajectories are converged, with the maximum variance of potential energy within 7 meV/atm, marking proper equilibration of the system.

The system preparation: For the THF solvent, the supercell of 8.9 Å × 15.4 Å × 14.6 Å is built and contains 16 THF molecules to be equivalent to the THF density of 884.6 Kg m^{-3} at the ambient conditions. 1 $LiBF_4$ molecule is added in the THF solvent to be equivalent to 0.5 M $LiBF_4$ in the solvent systems.

Data availability

All data are available in this article and its Supplementary Information. Source data are provided with this work.

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Author contributions

S.L., Y.Z., J.N. and I.C. conceived the paper. S.L. conducted the electrochemical experiments, collected and analysed SEM and XPS data. Y.Z. performed the theoretical calculation. X.F. contribute to the IC measurements and electrochemical experiments. J.B.P. and S.L. did the operando mass spectrometry experiments. M.S. carried out XRD measurements. K.E.R. did the NMR measurement. P.K., C.D.D. and S.L. conducted the cryo-TEM experiments and data analysis. S.Z.A., A.X., R.S., J.B.V.M., N.H.D., J.K. and P.C.K.V. contributed to the data analysis and discussion. S.L. Y.Z. J.N. and I.C. co-wrote the manuscript. All authors discussed the results and assisted during manuscript preparation.

Competing interests

Patent application titled “Flow cell for electrochemical ammonia synthesis” was submitted on 09-09-2022 (application number: EP22194879) regarding the reported diglyme solvent in the paper. Inventors: M.S., J.B.P., X.F., S.Z.A., R.S., S.L., Y.Z., K.L., J.K., P.C.K.V., J.K.N., I.C. J.B.V.M, N.H.D. Institution: DTU. The authors except M.S. and S.Z.A., declare no financial conflicts. M.S. and S.Z.A. declare the following competing interests: they have equity ownership in NitroVolt ApS, a Danish company working on commercializing electrochemical ammonia synthesis.

Additional information

Supplementary Information is available for this paper.

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