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Crystallographic Orientation of the Substrate Enables Micromole-Level Lithium-Mediated Ammonia Synthesis at 500 mA cm⁻²

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Abstract

The transition of the lithium-mediated nitrogen reduction reaction (Li-NRR) toward industrial application remains a formidable challenge. Achieving stable operation under ampere-level current density is particularly pivotal in this regard. An ideal solid-electrolyte interphase (SEI) plays a decisive role in determining the overall efficiency and feasibility. Current research predominantly focuses on bulk electrolyte optimization for SEI control, leaving the direct tailoring of electrode interphase underexplored. This lack of fundamental understanding hinders the achievement of highly efficient and stable Li-NRR toward practical application. Here, we report a strategy to atomic-scale restructure the interfacial microenvironment by engineering Cu substrates with a predominant (220) facet, leveraging the crystallographic orientation to present a definitive pathway for stable interphase. The Cu (220) facet selectively promotes the specific adsorption of anions within the inner Helmholtz plane (IHP), establishing a locally concentrated anion microenvironment even within dilute electrolytes. This facet induced enrichment overrides conventional reduction pathways dominated by solvents, triggering a kinetically accelerated evolution of a thin, robust SEI rich in inorganic components composed primarily of LiF and Li₂S. This tailored interphase architecture enhances the

interfacial Li^+ diffusion coefficient by two orders of magnitude and shortens the N_2 transport pathway, effectively balancing the transport of Li^+ , N_2 and H^+ , enabling the system to sustain a remarkable $1.1 \mu\text{mol s}^{-1} \text{cm}^{-2}$ ammonia production rate at a sustained current density of -500 mA cm^{-2} . This work demonstrates that atomic scale manipulation of substrate crystallography can dictate macroscopic interphase chemistry, charting a robust and scalable pathway for high flux electrochemical synthesis.

Keywords: Lithium-mediated nitrogen reduction reaction, Solid-electrolyte interphase, Microenvironment, Substrate crystallographic, High-current density

1 Introduction

Ammonia (NH_3) is an indispensable foundation for modern agriculture and is emerging as a promising zero carbon hydrogen carrier (1-5). Global production relies almost entirely on the Haber Bosch process (6), but its harsh operating conditions incur massive energy consumption and severe carbon emissions (7, 8). Consequently, there is a compelling urgency to develop sustainable electrified alternatives. The Li-NRR reaction stands out as a highly viable pathway for ambient condition ammonia electrosynthesis (9, 10). However, the transition of this technology toward industrial scale implementation hinges on the ability to operate at high current densities (11-13). Under such high flux conditions, the failure of the SEI becomes a fundamental barrier. Severe parasitic reactions, including continuous electrolyte solvent degradation and the hydrogen evolution reaction, drastically deplete the FE (14, 15). During operation, the SEI forms at the electrode through the competitive decomposition of lithium salts, organic solvents, and proton donors (11, 16). An ideal SEI must physically suppress these parasitic reactions while orchestrating the precise flux of essential species. Therefore, resolving the structural instability of this interphase under intense ion flux is widely recognized as the ultimate key to unlocking efficient ammonia synthesis at industrial levels.

A consensus has emerged that tailoring the composition and microstructure of the SEI is crucial for improving ammonia synthesis efficiency (17). Specifically, a robust interphase capable of sustaining rapid ion transport relies fundamentally on the initial nucleation of inorganic networks derived from anion decomposition (18-21). Previous studies have employed localized high concentration electrolytes or sterically hindered solvents to reinforce the coordination between Li^+ and anions (21, 22). These approaches successfully promoted the formation of inorganic rich interphases and improved the FE. While the beneficial

effects of these inorganic networks are well established, current strategies rely primarily on bulk electrolyte modifications, leaving the direct tailoring of electrode surfaces underexplored. The SEI nucleates directly on the current collector, meaning that the structural integrity of this layer is determined by its initial growth at the substrate crystallography (23). Systematic investigations into modifying the current collector itself to direct the adsorption and decomposition of lithium salts remain scarce (24). This lack of fundamental understanding hinders the achievement of highly efficient and stable Li-NRR toward practical application.

Fundamentally, the nucleation and growth of SEI are governed by the local interfacial microenvironment. Therefore, leveraging the substrate crystallographic orientation as an atomic scale substrate to selectively enrich anions for robust inorganic network formation presents a definitive pathway to engineering stable SEI. Here, we report a strategy to restructure the interfacial microenvironment by engineering Cu current collectors with a predominant (220) crystallographic orientation (**Fig. 1**). This tailored surface serves as an active substrate that selectively promotes the specific adsorption of bis(fluorosulfonyl)imide anions (FSI⁻) within the IHP. This precise interaction establishes a locally concentrated anion microenvironment at the electrode even within conventional dilute electrolytes. As a result, this facet induced enrichment overrides conventional reduction pathways dominated by solvents and triggers a kinetically accelerated evolution of a dense SEI rich in inorganic components composed primarily of LiF and Li₂S. Experimental observations reveal that this crystallographic engineering effectively suppresses the excessive accumulation of organic species like lithium ethoxide and guarantees robust inorganic network formation. This tailored interphase architecture minimizes charge transfer resistance and enhances the interfacial Li⁺ diffusion coefficient by two orders of magnitude, while effectively balancing the transport of Li⁺, N₂ and H⁺. Consequently, the optimized system achieves an outstanding Faradaic efficiency (FE) of 82.6% and an energy efficiency of 22.7% at -4 mA cm⁻². Furthermore, under a demanding sustained cathodic current density of -500 mA cm⁻², the system maintains a remarkable Faradaic efficiency of 63.9% and an ammonia production rate of 1.1 μmol s⁻¹ cm⁻². This work demonstrates that atomic scale manipulation of substrate crystallography can dictate macroscopic interphase chemistry and provides a scalable pathway for high flux electrochemical synthesis.

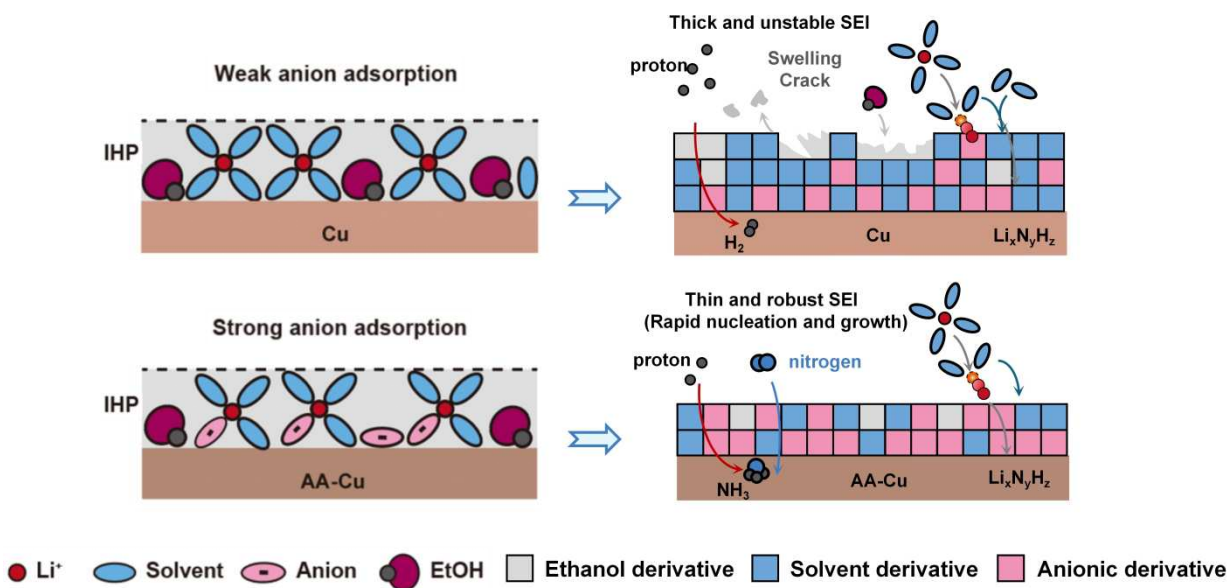


Fig. 1 | Schematic illustration of copper crystallographic orientation for a thin, robust SEI that enables a high-performance Li-NRR process.

2 Results and discussion

2.1 Crystal facet tailor of the copper substrate

Figs. 2a,b illustrate the successful fabrication of a Cu (220) crystal facet on a copper working electrode via simple electrochemical deposition in a saturated anionic environment. This facet, characterized by its high surface energy and abundance of active sites compared to others, generally demonstrates superior chemical and catalytic activity (25). Reports in the battery field indicate that sulfonyl groups specifically promote the preferential growth of the Cu (220) facet (26). The anion-preferring adsorption capability of this facet enables rapid anion reduction, leading to the formation of an inorganic-rich SEI (e.g., LiF, Li₂S). This approach effectively modulates SEI growth, composition, and structure, suppresses HER, enhances mass transport balance and selectivity in ammonia synthesis, and ultimately significantly improves synthesis performance. First, a pure copper foil was used as the counter electrode, while electrochemical deposition was performed on the working electrode (copper wire) using copper sulfate solutions containing different anion concentrations. The differences in the electrodeposition solutions are detailed in Supporting Information (solution status, **Supplementary Fig. 1**). Using this technique, we successfully fabricated a copper electrode dominated by the Cu (220) plane (Anion-Affinitive-Cu, AA-Cu), which served as a modified working electrode for lithium-mediated ammonia synthesis. The copper electrode was then characterized by X-ray diffraction (XRD) (27, 28). As shown in the XRD results (**Fig. 2c**), the pristine

copper surface (Cu) exhibited peak intensity ratios for Cu (111):Cu (200):Cu (220) of 1:0.67:1.71. In contrast, after electrochemical deposition with saturated anionic solution, the target copper surface (AA-Cu) appeared a significantly enhanced proportion of the Cu (220) crystal plane, with peak intensity ratios of Cu (111):Cu (200):Cu (220) reaching 1:0.71:7.63. Scanning electron microscopy (SEM) characterization further revealed the presence of Cu (220) facet surfaces on the modified copper electrode (**Fig. 2d**). This indicates that during the electrodeposition process, copper crystals preferentially grew along the (220) crystal plane, confirming the successful preparation of a modified copper electrode dominated by Cu (220) facets.

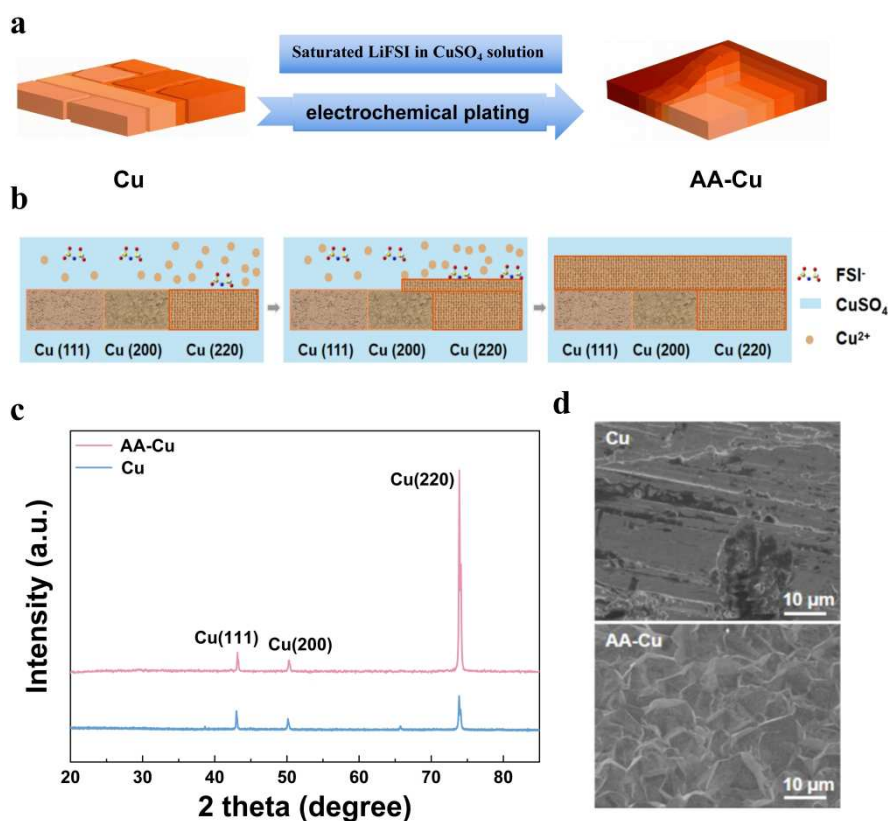


Fig. 2 | Preparation and characterization of the Cu (220)-textured working electrode (AA-Cu). **a**, Schematic of the electrochemical plating process converting Cu into AA-Cu in a saturated LiFSI/CuSO₄ solution. **b**, Schematic of the facet-selective growth process, showing progressive dominance of the Cu (220) facet over Cu (111) and Cu (200). **c**, XRD patterns of Cu and AA-Cu. **d**, SEM images of Cu and AA-Cu.

2.2 Trapped anions govern electrolyte decomposition pathways at metal–electrolyte interfaces

To begin with, three baseline electrolytes with varying concentrations of lithium bis(fluorosulfonyl)imide (LiFSI) in tetrahydrofuran (THF) were prepared, denoted as BE.1 (1 M LiFSI), BE.2 (1.5 M LiFSI), and BE.3 (2 M LiFSI). Subsequently, a localized high-concentration electrolyte (LHCE) was formulated based

on BE.3, consisting of 2 M LiFSI in a THF:TTE (1:1, v/v) solvent mixture, which is used for the subsequent comparison of ammonia synthesis performance. A series of electrochemical tests were then conducted using coin-type cells, primarily focusing on Coulombic efficiency (CE) measurements. The CEs obtained from Cu||Li half-cell tests are presented in **Supplementary Fig. 2**. Subsequently, the ionic conductivity of each electrolyte was tested (**Supplementary Fig. 3**). Among the four electrolytes, BE.1, BE.2, and BE.3 showed comparable ionic conductivities, which were about threefold higher than that of the LHCE electrolyte. Considering also the factor of cost-effectiveness, BE.1 was selected as the preferred base electrolyte for further study. Subsequently, the BE.1 electrolyte was also employed to comparatively evaluate the impact of the modified copper foil on enhancing the cycling reversibility of the lithium anode by measuring the CE (**Supplementary Fig. 4**) of lithium deposition and stripping in Li||Cu half-cells (29). These comparisons indicate that the SEI film formed on the modified copper foil is more uniform, stable, and results in less capacity loss (30). This suggests a significant improvement in the reversibility of lithium deposition/stripping during the initial SEI formation cycles, which can be attributed to the ability of the modified copper foil to preferentially adsorb anions and derive an inorganic-rich SEI structure (31). This further indicates that the predominant Cu (220) crystal phase on the surface of this modified copper foil enhances the cycling stability of lithium deposition and stripping.

To gain deeper insight into the non-Faradaic double-layer capacitive adsorption process within the inner Helmholtz plane (IHP), the adsorption behavior was further probed using alternating current voltammetry in the non-Faradaic potential region of 1.5–2.0 V. The adsorption capacitance was subsequently calculated from the data obtained via alternating current voltammetry. As shown in **Fig. 3a**, although the AA-Cu possesses a slightly lower surface positive charge density (indicated by a more negative potential of zero charge, E-PZC), its higher capacitance suggests that a greater number of anions can be arranged within its inner Helmholtz plane (IHP) at an identical potential to balance the surface charge. This points to an exceptionally strong intrinsic adsorption affinity of AA-Cu for anions. Such adsorption behavior underpins the design of anion-philic substrates to promote the stable formation of inorganic networks, thereby laying the groundwork for subsequent construction of a stable interface. At the same time, to experimentally verify the preferential adsorption of anions on the modified copper working electrode, differential capacitance measurements(9) was performed in the non-faradaic region (**Supplementary Fig. 5**). For differential capacitance determination by capacitive cycling, cyclic voltammograms (CV) were carried out in the autoclave at

different scan speeds ($10\text{--}80\text{ mV s}^{-1}$) from 0.2 mV to -0.2 mV vs OCV (**Supplementary Figs. 5a,b**). With this, a specific capacitance of $56.6\text{ }\mu\text{F cm}^{-2}$ was determined for the modified copper working electrode, and this is nearly half of the system before modification while the overall shape of the capacitance curve had changed (**Supplementary Fig. 5c**). This indicates that the FSI⁻ anions are more concentrated at the interface, leading to a rapid potential drop across the electric double layer. Combined with the steric hindrance effect, this results in a narrowing of the capacitance peak and a decrease in the capacitance value. The above results indicate that the copper crystal plane dominated by Cu (220) does indeed have anion affinity, which increases the interface capacitance.

To further confirm that the modified electrode effectively adsorbs anions and promotes their decomposition to form an anion-derived SEI, we conducted a 20-minute in situ FTIR test (32, 33) (**Figs. 3b,c and Supplementary Fig. 6**). After chronopotentiometric operation, the peak of anions on the modified Cu weakened progressively with time but was consistently more intense than that on the unmodified Cu. Concurrently, the weaker lithium ethoxide signal on the modified Cu suggests the effective suppression of the hydrogen evolution reaction. In comparison, the formation of a substantial black side product was observed in the in situ cell containing the bare Cu electrode. This effect thus contributes to greater stability of the SEI. These results collectively demonstrate that the modified electrode surface not only exhibits anion adsorption capability, promoting the formation of a stable SEI from the anions, but also thereby significantly suppresses side reactions during ammonia synthesis.

To elucidate the anomalous voltage rebound, potentiostatic intermittent titration technique (PITT) (34) with 0.05 V steps was employed, which is effective in determining nucleation overpotentials (**Figs. 3d-h and Supplementary Fig. 7**). A distinct current rise between 1.28 and 1.18 V was observed for the modified electrode (**Fig. 3d**), signaling the nucleation and growth of an anion-derived SEI. In contrast, the bare Cu electrode showed almost no such response in the range of 1.56 to 0.1 V (**Fig. 3e**), a result likely stemming from the strong affinity of its solvent-derived SEI for the electrolyte. The shape of the current transients agreed well with a nucleation and growth model, showing an initial phase of instantaneous nucleation with 3D growth that later transitioned to instantaneous nucleation with 2D growth (**Figs. 3f,g**). Besides, in modified copper AA-Cu, the lithium deposition capacity (35) is significantly increased, reaching $1.38 \times 10^{-2}\text{ mAh cm}^{-2}$, which is an order of magnitude higher than that of unmodified Cu (**Fig. 3h**). By combining these experimental results with the understanding of anion adsorption, it is reasonable to infer that a greater

number of anions participate in the interfacial reactions on AA-Cu, leading to the formation of a more robust SEI. In contrast, at the corresponding nucleation potential, the unmodified Cu likely involves fewer anions, resulting in an inferior SEI. The above experimental results demonstrate that the modified copper electrode surface facilitates the formation of an anion-derived SEI more rapidly. Initially, a uniform, dense, and continuous thin film is rapidly constructed. Subsequently, it evolves into a complete, thin, and homogeneous passivation layer. To verify the results, the experiments were reproduced with the electrolyte (with ethanol added) (**Supplementary Fig. 7**), and the obtained data were in full agreement with the findings presented above. This structural evolution more effectively suppresses parasitic reactions and stabilizes the electrode/electrolyte interface, thereby significantly enhancing the ammonia synthesis performance, especially at high current densities.

Then, cyclic voltammetry (CV) measurements (36) were conducted at various scan rates in the faradaic region (**Fig. 3i** and **Supplementary Figs. 8 and 9**). **Supplementary Fig. 8** shows a significantly stronger overall current response for AA-Cu, indicating its superior rate capability (i.e., better charge/discharge performance at high currents). The SEI formed on AA-Cu exhibits a substantially higher Li^+ diffusion coefficient of $3.16 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$, which is two orders of magnitude greater than that of the SEI from unmodified Cu ($7.01 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$) (**Fig. 3i**). This result supports the enhanced Li^+ transport kinetics at the AA-Cu electrode. The modified electrode likely facilitates a more favorable interfacial environment for nitrogen reduction. Its CV characteristics suggest a significantly attenuated reversibility of lithium deposition on this surface. Consequently, the deposited lithium species are expected to be more efficiently utilized for N_2 reduction rather than accumulating as metallic Li. This altered selectivity implies a greater potential of the system to divert current toward the nitrogen reduction reaction, which is anticipated to yield higher ammonia synthesis efficiency. Additionally, the Li^+ diffusion coefficients for the SEIs formed on modified and unmodified Cu substrates in the autoclave were measured. The SEI on the modified Cu exhibited a higher Li^+ diffusion coefficient than that of the SEI formed on the unmodified Cu. Those results corroborate the enhanced Li^+ transport property of the modified Cu electrode.

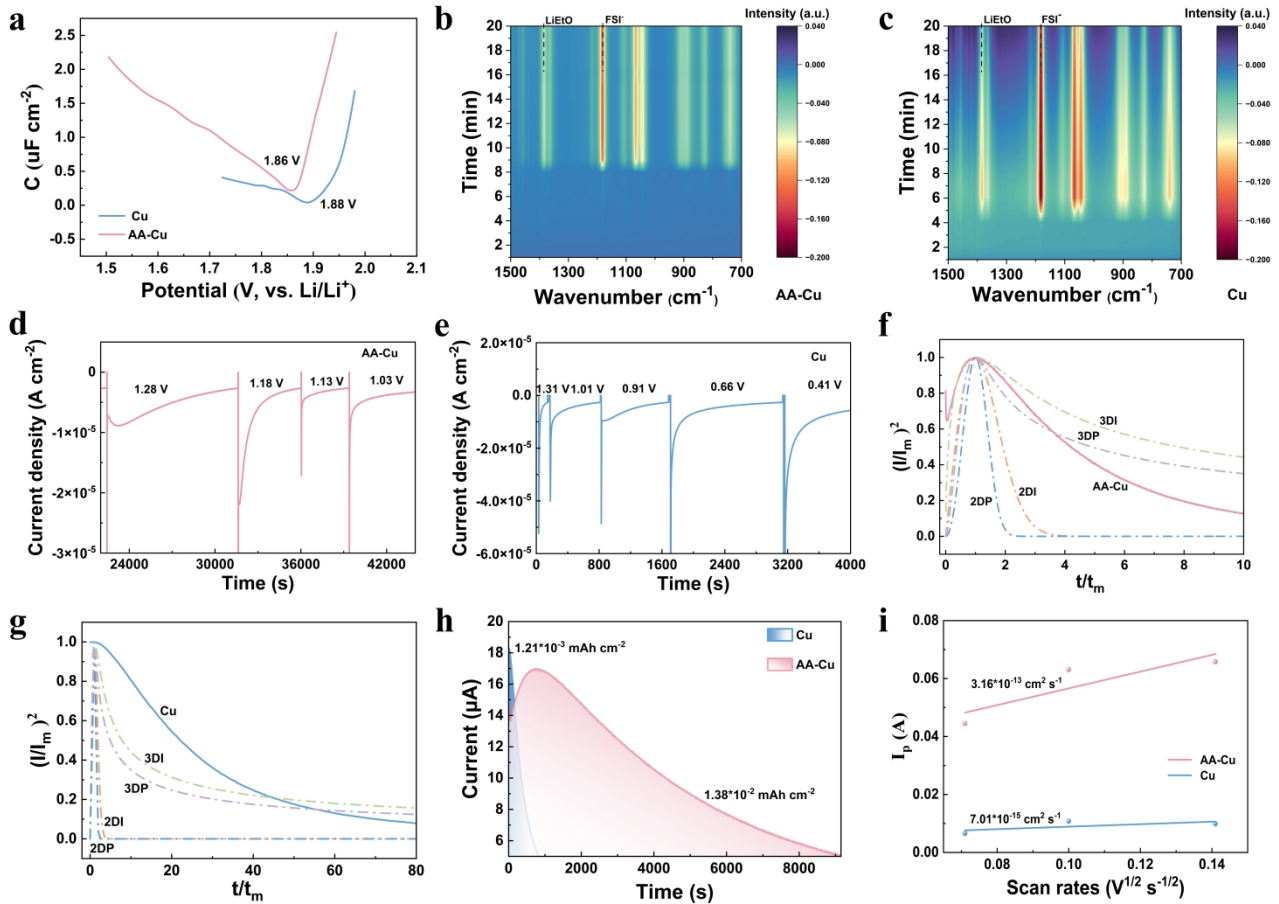


Fig. 3 | Anion affinity, interfacial ion transport and SEI nucleation/growth on AA-Cu versus Cu. **a**, Non-faradaic capacitance–potential curves for AA-Cu and Cu over 1.5–2.0 V (vs. Li/Li⁺). **b,c**, In situ FTIR spectra of the working electrode during CP measurements at -4 mA cm^{-2} for **b**, AA-Cu and **c**, Cu. **d,e**, PITT response currents under stepwise decreasing potentials near the reduction potential, in ethanol-free electrolyte, for **d**, AA-Cu and **e**, Cu. **f,g**, Normalized $(I/I_m)^2$ versus t/t_m plots (solid lines) compared with theoretical 2D and 3D nucleation models for **f**, AA-Cu and **g**, Cu. **h**, Chronoamperometric discharge curves of Li||Cu cells with AA-Cu and Cu at 25 °C, with integrated capacities indicated. **i**, Corresponding Li⁺ diffusion coefficients in the SEIs formed on AA-Cu and Cu, derived from the scan-rate dependence of the peak current.

2.3 Crystal facet-enhanced SEI boosts Li-NRR ammonia synthesis

To evaluate the impact of the designed modified copper electrode on the performance of lithium-mediated nitrogen reduction reaction (Li-NRR), electrochemical ammonia synthesis experiments were conducted in an autoclave under 20 bar of gas pressure (90% N₂ + 10% H₂). The electrolyte used was the base electrolyte BE.1, with 1 vol% EtOH serving as the proton source. Two sets of comparative experiments were performed using the modified copper electrode and the unmodified copper electrode as the working electrodes, respectively, a Pt electrode as the counter electrode, and a silver wire as the quasi-reference electrode. After

20 minutes at open-circuit voltage (OCV), linear sweep voltammetry (LSV) was initiated from the OCV until lithium deposition could be observed (**Supplementary Fig. 10**). Ammonia was then synthesized under a constant current density of -4 mA cm^{-2} . The working electrode potential and counter electrode potential measured over 10 hours of chronopotentiometry (CP) at -4 mA cm^{-2} are presented in **Supplementary Fig. 11** (Cu and AA-Cu). A key finding from the above LSV and chronopotentiometry (CP) measurements highlights that the modified working electrode facilitates rapid formation of a solid electrolyte interphase (SEI) and achieves a more positive lithium deposition potential, reaching -2.55 V . In addition, a distinct anion reduction peak appears approximately at -1.7 V . This change is beneficial to the stability of the SEI and holds promise for higher EE (37). Following the 10-hour CP test, electrochemical impedance spectroscopy (EIS) was conducted to determine the impedance (**Supplementary Fig. 12**). The modified copper electrode exhibited a smaller semicircle and a steeper slope in the Nyquist plot compared to the unmodified electrode, indicating reduced side reactions, promoted effective charge transfer, and lower interfacial impedance (38). Subsequently, cyclic voltammetry (CV) was performed to observe lithium deposition and stripping (39) (**Supplementary Fig. 13**). A more detailed description of the experimental procedure can be found in the SI. As revealed by the CV curves, the onset potential for lithium deposition on the modified copper electrode was significantly improved, suggesting the rapid formation of a superior SEI. More notably, the modified copper electrode demonstrated a higher reduction current density and smoother curves, validating that the hydrogen evolution reaction (HER) was effectively suppressed compared to the unmodified electrode. This resulted in more active lithium deposition and indicated higher intrinsic activity towards Li-NRR for the modified copper electrode. In the CV curves, the modified copper electrode showed larger peak areas for lithium deposition/stripping, suggesting that it more readily facilitates the protonation of lithium nitride to generate NH_3 and Li^+ , potentially promoting Li^+ nucleation.

After the chronopotentiometry tests, the NH_3 production was quantified using the UV-vis salicylate method (40), with the corresponding standard curves plotted in **Supplementary Fig. 14**. For comparison, the ammonia synthesis performance was also evaluated in a localized high-concentration electrolyte (LHCE) system using an unmodified electrode (**Supplementary Figs. 15-17**). Compared to the unmodified electrode, the system employing the LHCE combined with the modified electrode exhibited an enhanced Faradaic efficiency alongside a noticeable reduction in by-products on the copper wire surface. This, on the one hand, confirmed the universality of the modified copper electrode in different electrolyte systems. On the other

hand, the FE result of the LHCE system before modification was relatively close to those of the BE.1 system after modification, which once again reflects the anionic affinity of the modified electrode from the side. Furthermore, inspired by a previous study (10), the Pt counter electrode was replaced with a Pt/Au alloy counter electrode to further enhance the synthesis performance, and additional experiments were conducted (**Figs 4a-c and Supplementary Fig. 18**). The results indicate that the integration of the modified copper working electrode (WE) with a PtAu counter electrode led to a further increase in the working electrode potential while simultaneously decreasing the counter electrode potential, resulting in a low overall cell voltage of only -3.08 V. Following the 10-hour CP test, electrochemical impedance spectroscopy (EIS) was conducted to determine the impedance (38) (**Fig. 4b**). The modified copper electrode also exhibited a smaller semicircle and a steeper slope in the Nyquist plot compared to the unmodified electrode, indicating reduced side reactions, promoted effective charge transfer, and lower interfacial impedance. Furthermore, the cyclic voltammetry (CV) curves (**Fig. 4c**) showed no significant signs of the hydrogen evolution reaction (HER). Additionally, the electrolyte remained clear and transparent after a 10-hour chronopotentiometry (CP) test, in sharp contrast to observations in previously studied systems. These findings indicate a significant suppression of side reactions at both the WE and CE in this system. The FE, ammonia yield, and energy efficiency measured over 10 hours at -4 mA cm^{-2} for four different electrolytes (each with 1 vol% EtOH as the proton source) are summarized in **Figs. 4d,e and Supplementary Figs. 19 and 20**. The experimental results demonstrate that the FE of Cu working electrode for ammonia production at -4 mA cm^{-2} reached twice that of the AA-Cu working electrode. Furthermore, by employing the modified working electrode in combination with a Pt/Au electrode (10), an FE of 82.6% was achieved, with an energy efficiency of 22.7%. Additionally, the BE.1 electrolyte remained clear and transparent with negligible color change after the CP test (**Supplementary Figs. 21a and 21c**), indicating significant suppression of solvent decomposition. Correspondingly, the surface of the modified copper wire appeared relatively clean after CP, whereas substantial deposits were observed on the unmodified copper wire surface (**Supplementary Figs. 21b and 21d**). These results demonstrate that modifying the copper wire working electrode effectively suppresses side reactions such as HER, protects the lithium metal and lithium alkoxide phases, enhances the overall mass transport balance, improves the selectivity for ammonia synthesis, and consequently leads to significantly enhanced overall ammonia synthesis performance. The control experiments to confirm the nitrogen source (**Fig. 4f**). Finally, the contrast of systems under nitrogen versus argon atmospheres indicated that the

generated ammonia was derived from the supplied nitrogen. Notably, CP was conducted at a constant current density of -500 mA cm^{-2} (**Figs. 4g,h**). The system exhibited remarkable stability for about 26 minutes, retaining an FE of 63.9% and achieving an ammonia production rate of $1.1 \text{ } \mu\text{mol s}^{-1} \text{ cm}^{-2}$. The results indicate that the modified system yields a more robust and advantageous SEI, which effectively balances the relative diffusion kinetics of the reactants (Li^+ , N_2 , H^+). This balanced mass transport thereby grants the system exceptional stability at high current densities, leading to a substantial improvement in the ammonia synthesis rate.

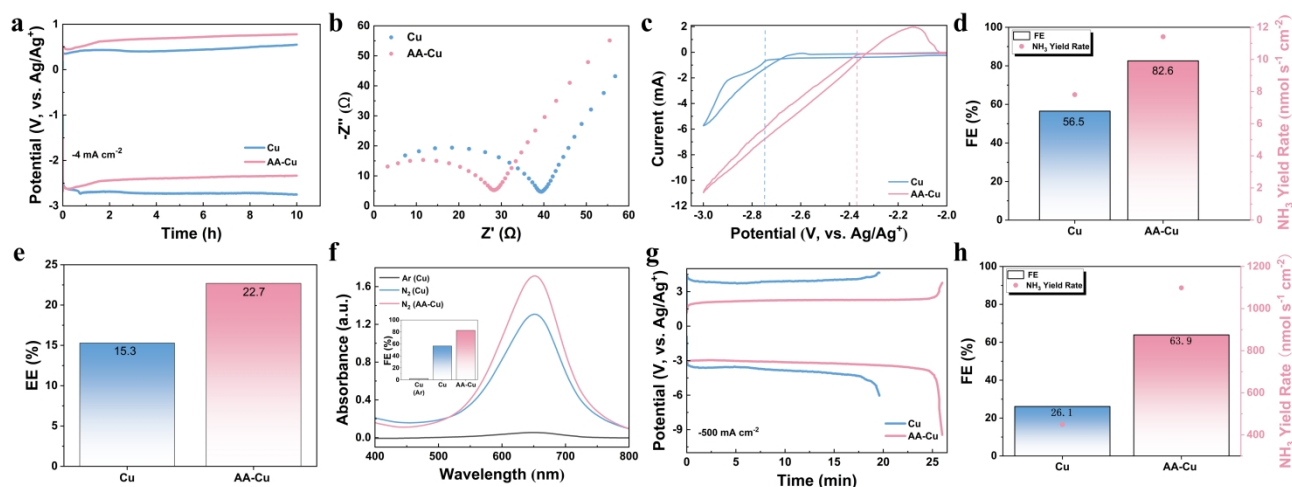


Fig. 4 | Li-NRR performance on Cu and AA-Cu. **a**, Potential profiles during CP measurements at -4 mA cm^{-2} (with PtAu counter electrode). **b**, EIS spectra of Cu and AA-Cu. **c**, CV curves of Cu and AA-Cu. **d**, FE and NH_3 yield rate at -4 mA cm^{-2} . **e**, Energy efficiency under the same conditions as in **d**. **f**, Ammonia source test comparing N_2 - and Ar-fed CP tests at -4 mA cm^{-2} (inset, FE). **g**, Potential profiles during CP measurements at -500 mA cm^{-2} (with PtAu counter electrode). **h**, FE and NH_3 yield rate at -500 mA cm^{-2} .

2.4 Characterization of the electrode-electrolyte interface

To elucidate the intrinsic mechanisms underlying the significant performance differences between the unmodified and modified copper electrodes, the research team systematically characterized the SEI formed on both electrodes. SEM was employed to examine the SEI morphology (41), X-ray photoelectron spectroscopy (XPS) to analyze its composition (**Figs. 5a-c and Supplementary Fig. 22**). The SEM images in **Figs. 5a,b** revealed distinct interfacial morphological differences. In the BE.1 unmodified copper electrode system, the SEI exhibited an uneven, rugged surface with numerous large corrosive pits, which clearly failed to effectively prevent side reactions between the lithium metal and the electrolyte, ultimately

leading to inefficient ammonia synthesis. In contrast, a relatively dense, uniform, and flat SEI layer was formed in the modified copper electrode system. Closer observation revealed uniformly distributed fine nanoparticles on its surface, indicating excellent mechanical integrity and barrier properties. This SEI structure not only effectively mitigated side reactions but also facilitated efficient N_2 transport and subsequent proton activation, significantly enhancing the ammonia synthesis performance. Further analysis of the SEI via XPS highlighted differences in the proportion and type of inorganic components between the two electrolytes and the two electrode states (42) (**Fig. 5c**). Specifically, the F 1s and Li 1s spectra showed that the peak intensities corresponding to LiF and Li_2S were significantly higher in the modified copper electrode system, indicating more sufficient formation of an inorganic-rich SEI. Among them, Li_2S has superior ionic conductivity (43). Concurrently, a distinct Li^0 peak was observed in the unmodified system, suggesting the presence of dead lithium, which also indirectly reflects that this portion of lithium could not effectively interact with N_2 and protons for ammonia synthesis. Furthermore, the O 1s spectrum demonstrated that the ROLi peak intensity was markedly weaker in the modified electrode system, indicating the formation of much less insoluble lithium ethoxide species, which are beneficial for balancing N_2 transport and enhancing ammonia synthesis performance.

The effect of this induced inorganic-rich SEI is similar to that achieved by localized high-concentration electrolytes. Systematic experiments indicate that the induced Cu (220) crystal plane readily adsorbs electrolyte anions, promoting their reduction to form an SEI rich in LiF and Li_2S . This optimized anion-derived SEI, characterized by its inorganic-rich composition, not only effectively protects the lithium metal and lithium ethoxide phases but also suppresses side reactions, while ensuring efficient N_2 transport and proton activation. Ultimately, the NRR performance was significantly enhanced.

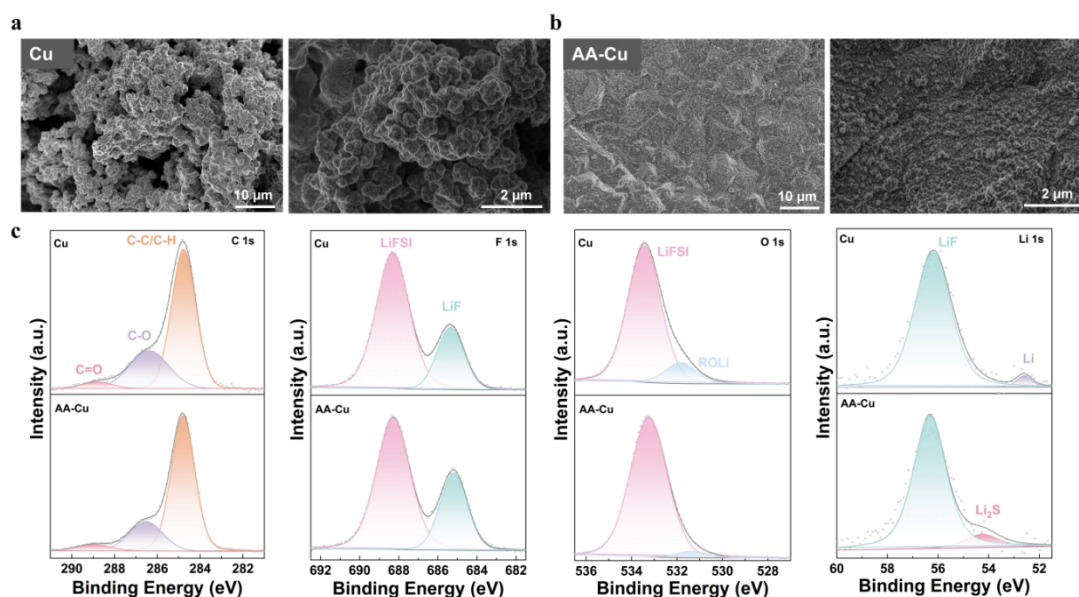


Fig. 5 | Analysis of SEI components and structural changes after 10 hours of ammonia synthesis. a,b, SEM images showing the surface morphology of a, Cu and b, AA-Cu. c, XPS profiles of C 1s, F 1s, O 1s and Li 1s for deposits on the working electrode of Cu and AA-Cu.

3 Conclusion

In this study, we employed a strategy of microenvironment engineering on the copper electrode to create an anion-affinitive substrate, which fostered a robust SEI and thus enabled a high-performance Li-NRR process. It confirmed that the modified copper electrode preferentially adsorbs anions during the initial formation of SEI. This promotes the rapid reduction of anions, leading to the derivation of an SEI rich in inorganic components like LiF and Li₂S. This synergistic strategy optimizes the growth kinetics, composition, and structure of the SEI, concurrently suppressing excessive lithium ethoxide formation, reducing charge-transfer resistance. It is worth mentioning that the tailored interphase architecture enhances the interfacial Li⁺ diffusion coefficient by two orders of magnitude and effectively balances the transport of Li⁺, N₂ and H⁺. The resultant effect is a significant boost in nitrogen reduction reaction performance, especially under high-current-density conditions. As anticipated, the system achieves a remarkable FE of 82.6% and an energy efficiency of 22.7% at -4 mA cm⁻². Moreover, the optimized system achieves an FE of 63.9% with a sustained current density of -500 mA cm⁻² and an NH₃ production rate of 1.1 μmol s⁻¹ cm⁻², leading to a remarkable improvement in ammonia synthesis performance. Therefore, exploring rational modification strategies for the working electrode to directly regulate the SEI represents a worthwhile research direction.

This work provides a novel design concept for highly selective electrodes in future Li-NRR systems.

Acknowledgments

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