Supporting Information

Nitrate-to-Ammonia Conversion at an InSn-Enriched Liquid-Metal Electrode

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Materials

Gallium, galinstan, nitric acid, hydrochloric acid, potassium nitrate, potassium nitrate (N15-labelled) and sodium nitrite were purchased from Sigma Aldrich. Copper foil was purchased from Goodfellow and deuterium oxide was purchased from NOVA chemicals. All chemicals were used as received.

Working electrode fabrication

Initial experiments were conducted using a 1g droplet of gallium or galinstan as the working electrode in a three-electrode cell set-up. To maintain the liquid state of the working electrodes each sample was heated to 50°C. To test a larger surface area gallium and galinstan were allowed to wet copper foil. The copper foil was cleaned in nitric acid, ethanol, acetone and MilliQ water by sonication for 10 minutes each and then dried using N₂ gas. It was then submerged in 1M hydrochloric acid. Galinstan was then dropped into a petri dish and allowed to touch the copper foil. Instant adhesion and wetting was achieved across a measurable surface area. Kapton tape was used to mask the areas of the foil where Galinstan adhesion was not wanted.

Materials characterisation

The GaInSn film on Cu was analysed using a Zeiss Sigma Scanning Electron Microscope using Energy Dispersive X-rays Spectroscopy to analyse composition using Point and ID and mapping analysis methods. The electrode was used to conduct nitrate reduction for 1 hour and then washed with water, dried with nitrogen and analysed again for composition changes within the liquid metal droplets.

Electrochemical nitrate reduction

Electrochemical nitrate reduction was completed using two electrochemical cell set-ups. To connect the liquid metal to the potentiostat a 50mL falcon tube was pierced at the bottom using a needle. The needle would connect to the liquid metal droplet sitting on the inside of the tube while the potentiostat was connected externally. The acids (HNO₃, H₂SO₄) were prepared in standard volumetric flasks from concentrated chemical stock, then diluted using MilliQ water to the appropriate concentration. The electrolyte used was 5mL of 0.1M HNO₃ with a Ag/AgCl
reference electrode and a carbon rod counter electrode. Cyclic voltammetry was used to compare the currents obtained from -0.5 to -1.4 V vs Ag/AgCl between HCl and HNO₃ electrolytes in order to determine the best potentials to run chronoamperometry experiments. The chronoamperometry experiments were run using the same electrochemical set-up however the potential was held at -1.25 V vs Ag/AgCl for 8 hours. It is important to note these experiments couldn’t be stirred as the liquid metal droplet is sitting at the bottom of the tube. This was then repeated at 50°C simultaneously using Galinstan and gallium to ensure ambient ammonia didn’t distort ammonia readings. Once it was confirmed that Galinstan and not gallium was able to reduce nitrates to ammonia a more robust set-up was used for electrochemical testing.

A three-electrode cell set-up was then used with the same electrodes, replacing liquid metal with the liquid metal copper electrodes. These experiments were stirred which increased rate of nitrate conversion to ammonia. Voltages were corrected from Ag/AgCl to RHE and current values corrected to current density values based on the surface area of the electrodes used.

Quantification of ammonia

To quantify the amount of ammonia produced from the electrochemical experiments, standards of NH₃ in HNO₃ were made and analysed using a 600MHz Bruker Avance Instrument with Sample Jet in oven dried glassware. Standard ammonia solutions were prepared by dilution in standard volumetric flasks using concentrations of ammonia from 25 to 1000 ppm in 0.1M HNO₃ in MilliQ water. 0.9 mL of each standard was then combined with 0.1 mL D₂O in a vial and then transferred to an NMR tube. Water suppression experiments were conducted using proton NMR with an acquisition time of 3.5 seconds using 64 scans. Mestrenova NMR analysis software was used to analyse all NMR samples. Each sample was baseline corrected, with peak intensity and integration measured for the ammonia peaks found. The same NMR sample preparation method was used for nitrate conversion to ammonia electrochemical experiments to accurately quantify ammonia. A calibration curve of each standard was made and it was found that using the integration proved more accurate for the determination of ammonia concentration as the intensity is dependent on the receiver gain parameter. To determine the rate and efficiency of the catalyst for nitrate conversion to ammonia, the following equations were used:

\[
Rate = \frac{(C_{NH3} \times V)}{(t \times Area)}
\]
Isotopic labelling

N-15 labelled KNO$_3$ was used to perform the isotopic labelling experiment. Although, previous reactions had been performed using nitric acid as the source of nitrate, N-15 labelled nitric acid was challenging to find. Before conducting the isotopic labelling experiment, the synthesised catalysts were tested for their ability to convert nitrate to ammonia using KNO$_3$ in the presence of H$_2$SO$_4$. 0.05M H$_2$SO$_4$ and 0.05M KNO$_3$ were combined and tested using the same electrochemical parameters described in the section Electrochemical Nitrate Reduction. KNO$_3$ and N-15 labelled KNO$_3$ solutions were prepared by using an analytical balance to weigh the solids, then transferred to a volumetric flask and dissolved in MilliQ water. The same experiment was then repeated using the isotopically labelled N-15 KNO$_3$ and NMR samples were prepared using the same method described in the section Quantification of Ammonia.

Computational Details:

The DFT-based first principle calculation was performed by Vienna Ab initio Simulation Package (VASP) \cite{1} \cite{2}. The Projector Augmented Wave (PAW) method \cite{3} was adopted to describe the interaction between the core and electrons with a cut-off of plane wave basis set as 400eV. The generalized gradient approximation (GGA) was used with the Perdew-Burke-ERNzerhof (PBE) form \cite{4} \cite{5}. In all calculations, the structures were firstly relaxed until the residual force decreased to 0.01eV/Å and energy convergence reached $10^{-5}$eV on all atoms. The slab model was built by a 4-layer (4*4) In$_3$Sn(100) supercell with the bottom two layer fixed to mimic the bulk properties, and a vacuum layer of 16Å was added to the model to exclude the interaction of adjacent images in z-direction. A grid of (2*2*1) kpoint was applied in all structural optimization calculations.

The surface energies of each slab model were calculated as below:

$$\sigma_{surf} = \frac{1}{2} \left( \frac{E_{unrel} - N_{cells} \times E_{bulk}}{N_{atoms}} \right) + \sigma_{rel}$$

where $E_{unrel}$ is the electronic total energy of unrelaxed slab, $N_{atoms}$ is the number of primitive cells in the slab model, $E_{bulk}$ is the average energy of one primitive cell in bulk materials and $\sigma_{rel}$ is the difference of total energy of the slab during structural relaxation. Following this formula, the surface energies of all low-index crystal surface of In$_3$Sn are calculated as Table S2:
For each electrochemical step, the change in Gibbs free energy was evaluated by the equation below:

\[ \Delta G = \Delta E + \Delta ZPE - T\Delta S + eU + \Delta G_{pH} \]

where \( \Delta E \) is the energy difference of DFT calculations of products and reactants on the slab model between steps, \( \Delta ZPE \) is the difference of zero-point energy of adsorbed intermediates. \( T\Delta S \) is the contribution of entropy. For adsorbed intermediates, the \( (\Delta ZPE - T\Delta S) \) term was calculated by VAPSKIT \(^6\) while it was obtained from NIST database \(^7\) for gaseous molecules. 
\( eU \) is the effect of external potential where \( U \) is the potential of electrode, and \( \Delta G_{pH} \) is correction of pH value which is evaluated as \( \Delta G_{pH} = k_B T \cdot pH \cdot \ln10 \). It’s obvious that the latter two terms don’t influence the relatively energetic difference of intermediates because they are fixed values, so we can set \( U=0 \) V vs. RHE and omit \( \Delta G_{pH} \) for all our calculations.

It’s worth noting that \( NO_3^- \) adsorption is the prerequisite for this reaction. To accurately calculation the free energy change during the adsorption process, we used the scheme proposed by Calle-Vallejo et al \(^8\):

\[ \Delta G_{ads}(NO_3^-)(l) = \Delta G_{ads}(NO_3^-)(vac) + 0.392eV \]

here 0.392eV is the difference of Gibbs free energy between gaseous HNO\(_3\) molecule and \( NO_3^- \) in aqueous solution.
Table S1. Comparison of different electrocatalysts used for the conversion of nitrate to ammonia.

| Sample                | Electrolyte                          | Rate          | Faradaic Efficiency (%) | Stability                                      |
|-----------------------|--------------------------------------|---------------|--------------------------|------------------------------------------------|
| GaInSn This work      | 0.1M HNO₃                            | 2335 µg NH₃ h⁻¹ cm⁻² | 100%                     | Stable for 10 cycles and 21 hours continuous electrolysis |
| Fe SAC⁹               | 0.5M KNO₃ + 0.1M K₂SO₄              | 8000 µg NH₃ h⁻¹ cm⁻² | 75%                      | 20 cycles at 1800 µg NH₃ h⁻¹ cm⁻²               |
| Pd-doped TiO₂⁹        | 1M LiCl + 0.25M LiNO₃               | 1120 µg NH₃ h⁻¹ cm⁻² | 92.1%                    | 550 µg NH₃ h⁻¹ cm⁻² for 12 hours               |
| Rh (100) surfaces on C¹¹ | 0.1M KOH + 0.1M KNO₃             | 34.4 µg NH₃ h⁻¹ cm⁻² | 20.8%                    | N/A                                            |
| Fe-PPy SACs¹²         | 0.1M KOH + 0.1M KNO₃               | 2750 µg NH₃ h⁻¹ cm⁻² | 100%                     | N/A                                            |
| CuCl_BEF¹³            | 0.5M Na₂SO₄ + 100ppm KNO₃           | 1820 µg NH₃ h⁻¹ cm⁻² | 95.6%                    | 7 cycles at >90% selectivity towards NH₃      |
| Cu nanosheets¹⁴       | 0.1M KOH + 170ppm NO₃⁻              | 390 µg NH₃ h⁻¹ cm⁻² | 99.7%                    | N/A                                            |
| Cu/Cu₂O NWA¹⁵         | 0.5M Na₂SO₄ + 200ppm NO₃⁻           | 4163 µg NH₃ h⁻¹ cm⁻² | 95.8%                    | 3399 µg NH₃ h⁻¹ cm⁻² after 6 hours             |
| CoP NA¹⁶              | 0.1M PBS + 500ppm NO₂⁻              | 2260 µg NH₃ h⁻¹ cm⁻² | 90%                      | Stable for 6 cycles                           |
| Co/CoO NSA$^{[17]}$ | 0.1 Na$_2$SO$_4$ + 200ppm NO$_3^-$ | 1650 $\mu$g$_{NH3}$ h$^{-1}$ cm$^{-2}$ | 93.8% | Stable for 5 cycles |
| CuNPs $^{[18]}$ | 0.5M K$_2$SO$_4$ + 50ppm NO$_3^-$ | 781 $\mu$g$_{NH3}$ h$^{-1}$ cm$^{-2}$ | 93.3% | Stable for 5 cycles |

**Table S2:** Calculated surface energy of In$_3$Sn with different indexes and termination

| Crystal index & termination | Surface energy (eV/Å$^2$) |
|-----------------------------|---------------------------|
| 100-In                      | 0.0189                    |
| 100-InSn                    | 0.0202                    |
| 111-InSn                    | 0.0237                    |
| 110-InSn                    | 0.0266                    |
| 110-In                      | 0.0290                    |

**Table S3:** Calculated surface energy of Ga$_2$Cu with different indexes and termination

| Crystal index & termination | Surface energy (eV/Å$^2$) |
|-----------------------------|---------------------------|
| 110-CuGa                    | 0.064                     |
| 111-CuGa                    | 0.088                     |
| 001-Cu                      | 0.098                     |
Figure S1. Schematic illustration of the working electrode synthesis and electrochemical nitrate reduction with NMR analysis performed on the electrolyte. It should be noted that is a schematic and the top of the cell was covered.

Figure S2. Long term stability test.
Figure S3: Digital image before and after electrolysis.

Figure S4. Schematic of preliminary experiments using a falcon tube setup to monitor the electrocatalytic activity of large scale Ga and GaInSn liquid drop electrodes at 50°C.
Figure S5. SEM image and EDX spectrum of GaInSn film on a Cu substrate after nitrate reduction for 1 hour in 0.1 M HNO$_3$ at -0.74V vs RHE.

Figure S6. Free energy diagram of nitrate reduction on Ga$_2$Cu-110.
Figure S7. Proton adsorption free energy on 100-InSn surface of In$_3$Sn with commercial Pt|C also plotted for reference. All possible adsorption sites possessed a large positive value, suggesting poor H$^+$ adsorption ability and thus poor HER performance.

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