Supplementary Information for

Ammonia-fed reversible protonic ceramic fuel cell with Ru-based catalyst

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Supplementary Table S1. Comparison of H₂- and NH₃-fed SOFC and PCFC performance

| Anode           | Electrolyte | Cathode | OCV (V) | MPD (mW·cm⁻²) | % of MPD | Temp. (°C) | Ref. |
|-----------------|-------------|---------|---------|---------------|----------|------------|------|
| Ni-BCZYYb       | BCZYBN (4 μm) | BCFZY   | 1.05    | 944           | 877      | 93         | 650  | This work |
| Ni-BCZYYb       | BCZYBN (4 μm) | BCFZY   | 1.02    | 944           | 877      | 93         | 650  | This work |
| Ni-BCZYYb       | BCZYBN (4 μm) | BCFZY   | 1.11    | 109           | 140      | 71         | 600  | This work |
| Ni-BCZYYb       | BCZYBN (4 μm) | BCFZY   | 1.06    | 109           | 140      | 71         | 600  | This work |
| Ni-BCZYYb       | BCZYBN (4 μm) | BCFZY   | 1.13    | 131           | 145      | 94         | 450  | This work |
| Ni-BCZYYb       | BCZYBN (4 μm) | BCFZY   | 1.11    | 131           | 145      | 94         | 450  | This work |
| Ni-YSZ          | YSZ (4.5 μm) + GDC (2-4 μm) | LSCF | 1.12    | 103           | 140      | 71         | 600  | 1         |
| Ni-SCD          | SDC (10 μm)  | BSCF    | 0.75    | 1872          | 1190     | 64         | 650  | 2         |
| Ni-SCD          | SDC (10 μm)  | BSCF    | 0.79    | 1357          | 434      | 32         | 600  | 2         |
| Ni-SCD          | SDC (10 μm)  | BSCF    | 0.82    | 748           | 167      | 22         | 550  | 2         |
| Pd foil (50 μm) | BZY (1 μm)   | LSCF    | 1.06    | 580           | 810      | 72         | 600  | 3         |
| Pd foil (50 μm) | BZY (1 μm)   | LSCF    | 1.08    | 340           | 490      | 69         | 550  | 3         |
| Pd foil (50 μm) | BZY (1 μm)   | LSCF    | 1.12    | 210           | 240      | 88         | 500  | 3         |
| Pd foil (50 μm) | BZY (1 μm)   | LSCF    | 1.13    | 71            | 85       | 84         | 450  | 3         |
| Ni-YSZ          | YSZ (15 μm)  | LSM-YSZ | 1.07    | 70            | 80       | 88         | 650  | 4         |
| Ni-BCE          | BCGO (1000 μm) | Pr    | 1       | 28            | 36       | 78         | 600  | 5         |
| Ni-YSZ          | YSZ (30 μm)  | LSM-YSZ | 1.08    | 91            | 94       | 86         | 650  | 6         |
| Ni-CGO          | BCGO (50 μm) | BSCFCGO | 1.11    | 90            | 223      | 90         | 600  | 7         |
| Ni-CGO          | BCGO (50 μm) | BSCFCGO | 1.14    | 85            | 172      | 147        | 600  | 7         |
| Ni-SCD          | SDC (24 μm)  | SSC-SDC | 0.8     | 54            | 870      | 467        | 600  | 7         |
| Ni-SCD          | SDC (24 μm)  | SSC-SDC | 0.84    | 51            | 580      | 295        | 600  | 7         |
| Ni-SCD          | SDC (24 μm)  | SSC-SDC | 0.88    | 57            | 300      | 170        | 550  | 7         |
| Fe²⁺/Ni-YSZ     | SSZ (15 μm)  | SSZ-LSM | 1.15    | 91            | 292      | 266        | 650  | 9         |
| Fe²⁺/Ni-YSZ     | SSZ (15 μm)  | SSZ-LSM | 1.15    | 98            | 286      | 279        | 650  | 9         |
| Ni-BZCY         | BZY (35 μm)  | BSCF    | -1.0    | 67            | 335      | 225        | 650  | 10        |
| Ni-BZCY         | BZY (35 μm)  | BSCF    | -1.0    | 68            | 280      | 190        | 600  | 10        |
| Ni-BZCY         | BZY (35 μm)  | BSCF    | -1.0    | 58            | 225      | 130        | 550  | 10        |
| Ni-BZCY         | BZY (35 μm)  | BSCF    | -1.0    | 56            | 180      | 65         | 500  | 10        |
| Ni-SCD          | SDC (50 μm)  | SSC-SDC | 0.87    | 88            | 192      | 168        | 600  | 10        |
| Ni-SCD          | SDC (50 μm)  | SSC-SDC | 0.93    | 79            | 82       | 79         | 600  | 10        |

Notes: 1) OCV: Open circuit voltage; 2) MPD: Maximum power density; 3) % of MPD: 100 x MPD(NH₃)/MPD(H₂); 4) YSZ: yttria-stabilized zirconia; 5) GDC: gadolinium-doped coria (CGO is used by authors in other references); 6) LSCF: La₂₀Ses²⁰Ce₀₂Fe₀₂O₇₋₈; 7) SDC: Ces₂Sn₂O₇₋₈; 8) BSCF: Ba₀₂Sn₀₂Ce₀₂Fe₀₂O₇₋₈; 9) BCFE: BaCe₀₂Fe₀₂E₀₂O₇₋₈; 10) BCGO: BaCe₀₂G₀₂O₁₉₃₆O₇₋₈; 11) CGO: Same as GDC; 12) BCGO: BaCe₀₂G₀₂O₁₉₃₆O₇₋₈; 13) BSCFCGO: Same as conventionally used BSCF; 14) SSC: Sm₀₂Se₀₂CoO₇₋₈; 15) Fe⁺²: 2 wt.% by impregnation Fe(NO₃)₃·H₂O and calcined at 600 °C; 16) SSZ: Ssc₁₂Zno₁₉; 17) BZY: BaZr₀₂Ce₀₂Y₀₂O₇₋₈; 18) SSC: Sm₀₂Se₀₂CoO₇₋₈; 19) BCZY: BaCe₀₂Zr₀₂Y₀₂O₇₋₈; 20) BCZYBN: BaCe₀₂Fe₀₂Zr₀₂Y₀₂O₇₋₈; 21) BCFZY: BaCe₀₂Fe₀₂Zr₀₂O₁₉₃₆O₇₋₈
Supplementary Table S2 Comparison of reported electrochemical ammonia production rate under ambient pressure (T* stands for this work)

| Catalyst | Negatrod e | Electrolyte | Postside | Proton Source | C# | NH₃ Rate mod s⁻¹ cm⁻² | Ref. |
|----------|------------|-------------|----------|--------------|----|------------------------|-----|
| Plasma   | Plasma     | H₂O-sulfuric acid | Pt       | H₂O          | 1  | 7.20E-07               | 12  |
| Li₃N     | Al         | LiCl-KCl-CrCl₃-LiCl | Ni       | H₂           | 1  | 3.33E-14               | 14  |
| Li₃N     | Ni         | LiCl-KCl-CrCl₃-LiCl | Carbon   | H₂O          | 1  | 2.00E-08               | 16  |
| Ru-BZCA  | Ni-BZCYb   | BZCYbN      | BZCY     | H₂O          | 2  | 1.20E-08               | T*  |
| SFCN     | SFCN       | Nafion      | Ni-SDC   | H₂           | 2  | 1.13E-08               | 18  |
| SSN      | SSN        | Nafion      | Ni-SDC   | H₂           | 2  | 1.05E-08               | 20  |
| Ag-Pt    | SSN        | Nafion      | Ni-SDC   | H₂           | 2  | 1.05E-08               | 22  |
| SSN      | SSN        | SPSF        | Ni-SDC   | H₂           | 1  | 1.03E-08               | 20  |
| Ag-Pd-SBCN | SBCN     | Nafion      | Ni-SDC   | H₂           | 2  | 8.70E-09               | 23  |
| Ag-Pd    | Ag-Pd      | CSO         | Ag-Pd    | H₂           | 2  | 8.20E-09               | 24  |
| Ag-Pd    | Ag-Pd      | CGO         | Ag-Pd    | H₂           | 2  | 7.70E-09               | 24  |
| Ag-Pd    | Ag-Pd      | CYO         | Ag-Pd    | H₂           | 2  | 7.50E-09               | 24  |
| Ag-Pd-SBCC | SBCC     | Nafion      | Ni-SDC   | H₂           | 2  | 7.30E-09               | 23  |
| Ag-Pd    | Ag-Pd      | CIA         | Ag-Pd    | H₂           | 2  | 7.10E-09               | 24  |
| Ag-Pd-SBCC | SBCC     | Nafion      | Ni-SDC   | H₂           | 2  | 7.00E-09               | 23  |
| Ag-Pd    | Ag-Pd      | Oxide-salt  | Ag-Pd    | CH₄          | 2  | 6.95E-09               | 31  |
| Ag-Pd    | Ag-Pd      | BCGS        | Ag-Pd    | H₂           | 2  | 5.82E-09               | 32  |
| LSFcu-SADC | LSFcu-SADC | Carbonate-SADC | Ni-SDC | H₂/O₂       | 2  | 5.39E-09               | 34  |
| Ag-Pd    | Ag-Pd      | BCS         | Ag-Pd    | H₂           | 2  | 5.23E-09               | 32  |
| Ag-Pd    | Ag-Pd      | BCC         | Ni-BCCO  | H₂           | 2  | 4.63E-09               | 37  |
| Pd       | Pd         | SCY         | Pd       | H₂           | 2  | 4.50E-09               | 38  |
| Ag-Pd    | BSCF       | BCY15       | Ni-BZCY  | H₂           | 2  | 4.10E-09               | 40  |
| Cu       | Cu         | BZCY        | Ni-BZCY  | H₂           | 2  | 4.10E-09               | 19  |
| Ag-Pd    | Ag-Pd      | BCD         | Ag-Pd    | H₂           | 2  | 3.50E-09               | 43  |
| Ag-Pd    | Ag-Pd      | BCG         | Ag-Pd    | H₂           | 2  | 3.09E-09               | 45  |
| Ru       | Ru         | BZCY27      | Ni-BZCY  | H₂           | 1  | 2.86E-09               | 46  |
| Ag-Pd    | Ag-Pd      | BCC         | Ni-BZCY  | H₂           | 2  | 2.69E-09               | 47  |
| Ag-Pd    | Ag-Pd      | BCZS        | Ag-Pd    | H₂           | 2  | 2.67E-09               | 49  |
| Ag-Pd    | Ag-Pd      | BCD         | Ag-Pd    | H₂           | 2  | 2.60E-09               | 51  |
| Ag-Pd    | Ag-Pd      | LGSM        | Ag-Pd    | H₂           | 2  | 2.17E-09               | 53  |
| Ag-Pd    | Ag-Pd      | BCCN        | Ag-Pd    | H₂           | 2  | 2.16E-09               | 13  |
| Ag-Pd    | Ag-Pd      | BCA         | Ag-Pd    | H₂           | 2  | 2.10E-09               | 56  |
| Ag-Pd    | Ag-Pd      | LCZ         | Ag-Pd    | H₂           | 2  | 2.00E-09               | 57  |
| Ag-Pd    | Ag-Pd      | BZC         | Ag-Pd    | H₂           | 2  | 1.92E-09               | 13  |
| Ag-Pd    | Ag-Pd      | LGSM        | Ag-Pd    | H₂           | 2  | 1.89E-09               | 15  |
| Ag-Pd    | Ag-Pd      | LGSM        | Ag-Pd    | H₂           | 2  | 1.82E-09               | 13  |
| Ag-Pd    | Ag-Pd      | LCZ         | Ag-Pd    | H₂           | 2  | 1.76E-09               | 17  |
| Cu       | Cu         | BZCY        | Ni-BZCY  | H₂           | 2  | 1.70E-09               | 19  |
| VN-Fe    | VN-Fe      | BZCY81      | Ni-BZCY  | CH₄          | 2  | 1.67E-09               | 21  |
| Ag-Pd    | Ag-Pd      | BCN         | Ag-Pd    | H₂           | 2  | 1.64E-09               | 13  |
| Ag-Pd    | Ag-Pd      | BCN         | Ag-Pd    | H₂           | 2  | 1.43E-09               | 13  |
| Ag-Pd    | Ag-Pd      | BCN18       | Ag-Pd    | H₂           | 2  | 1.42E-09               | 13  |
| Pt       | Pt         | Pt-C        | Nafion   | H₂O          | 2  | 1.14E-09               | 25  |
| Pt       | Pt         | Pt-C        | Nafion   | H₂O          | 2  | 9.37E-10               | 26  |
| LSCF-CGDC | LSCF-CGDC | Carbonate  | SSO-CGDC | H₂           | 2  | 4.08E-10               | 27  |
| Ag-CMN   | Ag-CMN     | Carbonate   | Ag-Pd    | H₂           | 2  | 3.27E-10               | 28  |
| Ag-CF    | Ag-CF      | Carbonate   | Ag-Pd    | H₂           | 2  | 2.32E-10               | 29  |
| Fe₃Mo₃N | Fe₃Mo₃N-Ag | Carbonate  | Ag-Pd    | H₂           | 2  | 1.89E-10               | 30  |
| Ag-Pd    | Ag-Pd      | CSO         | Ag-Pd    | H₂           | 2  | 1.83E-10               | 24  |
| PBCu     | PBCu       | Carbonate-CGO | PBCu   | H₂O          | 1  | 1.83E-10               | 33  |
| LCFN     | LCFN       | Carbonate-CGO | LCFN   | H₂O          | 1  | 9.21E-11               | 39  |
| LSCF-CGCa | LSCF-CGCa | Carbonate-CGCa | SSO-CGDC | H₂O         | 2  | 1.50E-10               | 36  |
| PBCu     | PBCu       | Carbonate-CGO | PBCu   | H₂O          | 1  | 1.07E-10               | 33  |
| LCFN     | LCFN       | Carbonate-CGO | LCFN   | H₂O          | 1  | 9.21E-11               | 39  |
| LSCF-CGCa | LSCF-CGCa | Carbonate-CGCa | SSO-CGDC | H₂O         | 2  | 5.00E-11               | 34  |
| Ag       | Ag         | BZY         | Ag      | H₂O          | 2  | 4.98E-11               | 41  |
| Pt       | Pt         | GDC         | Pt      | H₂O          | 2  | 3.67E-11               | 48  |
| Ag-Pd    | Ag-Pd      | BCY10       | Pt      | H₂           | 2  | 2.80E-11               | 49  |
| Nano-Iron | -         | Ionic liquids | Ni      | H₂O          | 1  | 2.30E-11               | 52  |
| Ru       | Ru         | Nafion      | -       | H₂O          | 2  | 2.12E-11               | 54  |
| Fe       | Fe         | SZY         | Ag      | H₂           | 2  | 6.20E-12               | 55  |
| Ru/MgO   | Ag         | YSZ         | Pd      | H₂O          | 2  | 6.98E-14               | 58  |

Notes: C# stands for number of chambers. 1 means all gases from two electrodes are mixed in one chamber; 2 means postside and negatrod e gases are separated from each chamber.
Challenges on electrochemical ammonia synthesis

In general, there are two reaction mechanisms regarding electrochemical production of ammonia from nitrogen and hydrogen: the dissociative mechanism and the associative mechanism \(^{59-64}\). These mechanisms are well reported in literature, but with variable nomenclature. For convenience, the reaction mechanisms are reformatted as following.

I) Dissociative mechanism: In the dissociative mechanism, each \( \text{N}_2 \) molecule forms two \( \text{N} \) atoms directly upon adsorption on the surface site. These then capture three protons and three electrons from the reaction interface or the reaction medium.

\[
\begin{align*}
(N \equiv N)_{g} + 2S & \rightarrow 2S \\
N_{g} + 2S + 6H^+ + 6e^- & \rightarrow 2S \\
2S & \rightarrow 2S + 2NH_{3,g}
\end{align*}
\]  
(R1) (R2) (R3)

II) Associative mechanism

\[
\begin{align*}
(N \equiv N)_{g} + S & \rightarrow S \\
(N=\text{N})_{g} + S & \rightarrow S \\
(N=\text{NH})_{g} + S & \rightarrow S \\
(H=\text{NH})_{g} + S & \rightarrow S \\
(H=\text{NH})_{g} + S & \rightarrow S \\
(S = \text{NH})_{g} + S & \rightarrow S
\end{align*}
\]  
(R4) (R5) (R6) (R7) (R8) (R9)

\[
\begin{align*}
S & \rightarrow S + NH_{3,g} \\
S & \rightarrow S + NH_{3,g}
\end{align*}
\]  
(R10) (R11)
where \( S \) in the above reactions is an empty catalyst surface site, \( S^{(N=N)} \) indicates dissociated atomic nitrogen adsorbed on a surface site, \( S^{(H,N,H)} \) indicates molecular nitrogen adsorption on surface site, and \( S \) indicates molecular \( \text{NH}_3 \) attached to a surface site. Other intermediate products on surface sites are defined similarly. Rate and equilibrium constants are shown as \( k_s \) and \( K_s \), respectively.

The dissociation energy in R1 reaches 945.4 kJ.mol\(^{-1}\). Additionally, the electrochemical driving force does no effect\(^{59,61}\), so that \( \text{N}_2 \) dissociation is the highly unfavorable rate-determining step.

II) Associative mechanism: The first hydrogenation of nitrogen (R6) is the rate-determining step in the associative mechanism\(^{60,61,65}\). The activation energy is \( \sim 94.5 \) kJ.mol\(^{-1}\)\(^{60}\), one order of magnitude lower than that of the rate-determining step in the dissociative mechanism. This makes the associative mechanism more energetically favorable for electrochemical ammonia production.

Following the dissociative mechanism, Singh et al. proposed a model to predict rate of ammonia and hydrogen production based on Langmuir isotherms\(^{61}\). The two most-important reactions:

\[
\begin{align*}
    r_N &= k_N \frac{K_N}{K_H} \tilde{c}_{N_2} \\
    r_H &= k_H \tilde{c}_+ \tilde{c}_- 
\end{align*}
\]

where \( K \)'s are the bulk-to-near-surface equilibrium constants, \( k \)'s are rate constants, and \( \tilde{c} \)'s are bulk concentration. Note the term \( \tilde{c}_- \) is not meant to indicate a physical concentration but to account for cases where the electron transfer rate is limiting\(^{61}\). The rate-determining step of this model is the first hydrogenation step of \( \text{N}_2 \) (R5).

The above two equations indicate the rate of ammonia production is zeroth order in the electron and proton concentrations, while the rate of hydrogen production is first order in both electron and proton concentrations. The two equations suggest the ammonia production rate is non-electrochemically driven and the rate is nearly independent of electron and proton concentrations.

In order to increase selectivity, the electron and proton concentrations must be minimized in order to minimize the hydrogen evolution reaction (HER). Detailed strategies on improving ammonia selectivity are proposed Singh et al.\(^{61}\). By suppressing the protonic current in proton-conducting cells, the \( \text{H}_2 \) production rate is reduced, while the nitrogen-reduction rate or ammonia-production rate are nearly unaffected, thereby achieving a higher selectivity to \( \text{NH}_3 \). This has been observed in a few studies where higher ammonia selectivities were achieved under relatively low current densities\(^{52}\). Of course, this approach generally is accompanied by low ammonia production rate due to the low current densities. Simultaneously maintaining high rates of ammonia synthesis and conversion efficiency remains very challenging in practice since the activation barrier of HER is much less than that of NRR. Further, no metal catalyst provides better catalytic selectivity in NRR over HER.

Montoya et al. applied DFT calculations to study electrochemical ammonia synthesis on various metal catalysts\(^{66}\). Among the 11 elements explored (Re, Ru Rh, Co, Ni, Ir, Pt, Pd, Cu, Au, Ag),...
no catalyst demonstrated a more-negative limiting potential under HER than NRR. Rhenium had the minimum difference between HER and NRR, followed by Ru; both metals are good candidates for high-selectivity ammonia synthesis.

These thermodynamic, kinetic, and catalytic analyses all show that it is fundamentally very challenging to suppress hydrogen-evolution reaction while increasing the nitrogen reduction reaction. Low selectivity to NH₃ is more favorable by nature. While better catalysts with higher selectivity may be found for electrochemical production of ammonia, rethinking the integrated electrochemical H₂ production - ammonia thermocatalytic synthesis coupling may prove more efficient, where higher pressure operation is technically more feasible and unused hydrogen can be recycled back to the NH₃-synthesis reactor.
Supplementary Figure S1 | TEM-EDX full elemental map showing reasonable uniformity across 300-nm particles and evidence of Ru-B2CA core-shell structure.
**Supplementary Figure S2** | Photographs showing. 

**a.** SEM image of electrolyte surface via solid state reaction synthesis (SSRS) method, the electrolyte is relatively dense with small defects without affecting cell open circuit voltage or performance. 

**b.** Comparison of X-ray diffraction spectra of BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.1}$Yb$_{0.1}$Ni$_{0.04}$O$_{3-\delta}$ (BCZYYbN) synthesized by sol-gel method and BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.1}$Yb$_{0.1}$O$_{3-\delta}$ (BCZYYb) synthesized by solid-state reactive sintering (SSRS) (1 wt% NiO was added). Both samples were heat treated at 1450 °C for 12h. Peaks for both materials are well aligned with database records for BaCe$_{0.8}$Zr$_{0.2}$O$_{3-\delta}$. A slight secondary phase is observed in the SSRS material.
Supplementary Figure S3 | Photographs showing. a, Anode green pellets. b, Electrolyte layer deposition via spin coating. c, Electrolyte layer deposition via drop coating. d to f, Sintered half-cell. g, Cathode application on half-cells. h, Example of sealing via ceramabond (552-VFG). i, Example of compress sealing.
Supplementary Figure S4 | Representative EIS at two temperatures under H₂ and cracked NH₃ fuel cell mode.
Supplementary Figure S5 | Long term stability test of a cell for up to 1250 h under various testing conditions. For cracked NH$_3$ fuel with trace amount of NH$_3$, we found the degradation is less sensitive as compared with operation conditions such as discharge current density, humidity, and temperature.
Supplementary Figure S6| Stability test of cell without cracking catalyst and postmortem analysis. a, The cell voltage dropped to zero even under OCV mode after exposure to non-cracked NH₃ fuel. Both the ohmic and polarization resistance increased significantly after cell degraded, respectively by 83 and 50 times higher. b, Postmortem analysis shows the cell has a dense and about 25 µm thick electrolyte layer. No mechanic cracks in the electrolyte layer were found based on the measured areas. Note this cell has a drop coated electrolyte layer via SSRS process.
Supplementary Figure S7 | Additional and larger viewing field SEM images of assintered porous BCZYYb pellet (with 1 wt.% NiO).
Supplementary Figure S8| Additional and larger viewing field SEM images of porous BCZYYb pellets (with 1 wt.% NiO) after H₂ reduction.
Supplementary Figure S9 | Additional and larger viewing field SEM images of porous BCZYYb pellets (with 1 wt.% NiO) after NH₃ reduction.
Supplementary Figure S10 | Additional and larger viewing field SEM images of as-sintered porous NiO pellet.
Supplementary Figure S11| Additional and larger viewing field SEM images of porous NiO pellets after H2 reduction.
Supplementary Figure S12 | Additional and larger viewing field SEM images of porous NiO pellets after NH₃ reduction.
Supplementary Figure S13| Full electrochemical impedance spectroscopy (EIS) of a porous BCZYYb pellet (with 1 wt.% NiO) under N₂ flow and before switching to H₂ and NH₃.
Supplementary Figure S14| Anode nitridation verification experiment with exposure to NH$_3$ gas. Little evidence for formation of Ni$_3$N under the testing conditions.
Supplementary Figure S15 | Measured ammonia production rates as a function of total flow rate of 3:1 H$_2$ to N$_2$ gas mixture with comparison to equilibrium calculation. Reactor temperature at 400 °C.
Supplementary Figure S16 | Effect of hydrogen flux through the protonic-ceramic electrolyzer on ammonia-synthesis rate.
Supplementary Figure S17 | Illustrations of pressure test. a, packaging and sealing of the high pressure protonic-ceramic membrane-electrode assembly within b, electrochemical test stand and downstream ammonia-synthesis reactor.
Supplementary Figure S18| Ammonia detection and calibration.  a, a tested Drager tube showing the distinct color of NH$_3$ absorbed region (blue) and non-absorbed region (yellow)  b, linear plot of time reaching each specific marker position versus labelled marker to using 10 ppm NH$_3$ in N$_2$ standard gas.
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