Supplementary material for:

Combined effect of pressure and temperature on nitrogen reduction reaction in water.

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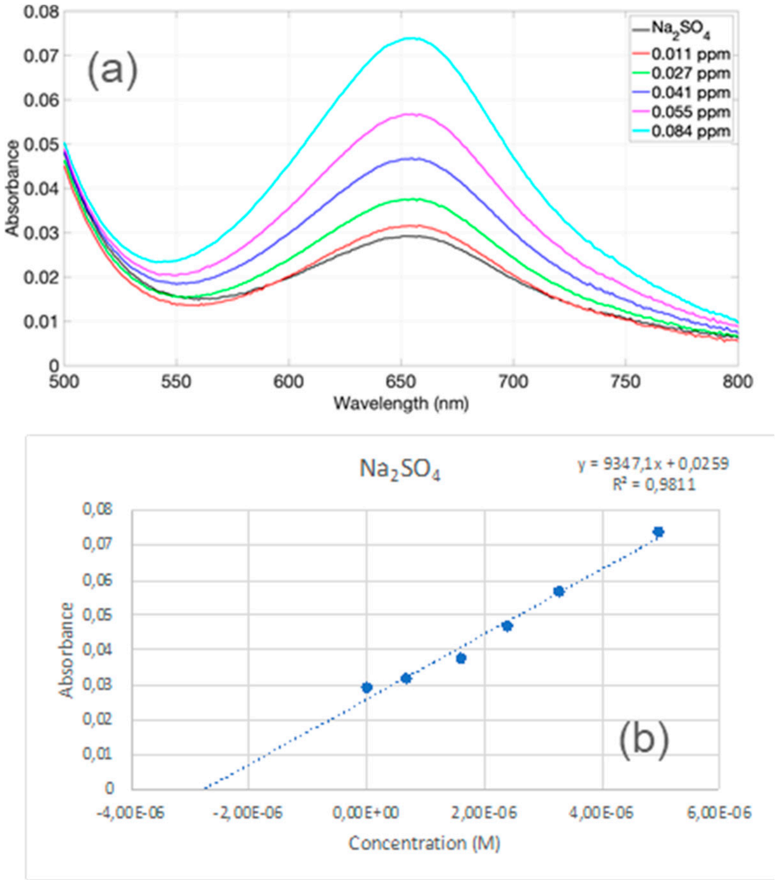

Figure S1: Typical calibration procedure adopted with the standard addition method: (a) absorbance spectra and (b) the corresponding calibration for standard ammonia solutions.

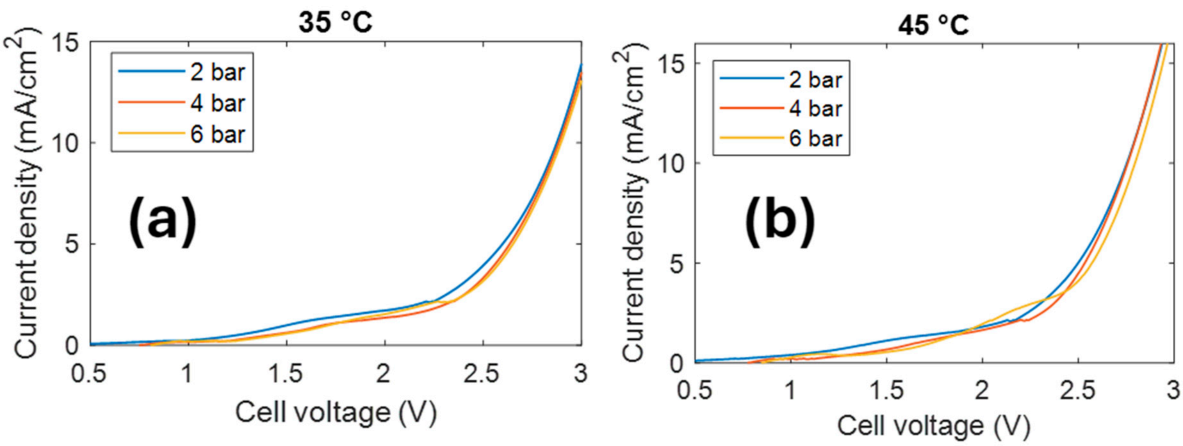

Figure S2: Linear sweep voltammetry curves acquired in the pressurized cell in saturated N_2 at different pressure and temperature.

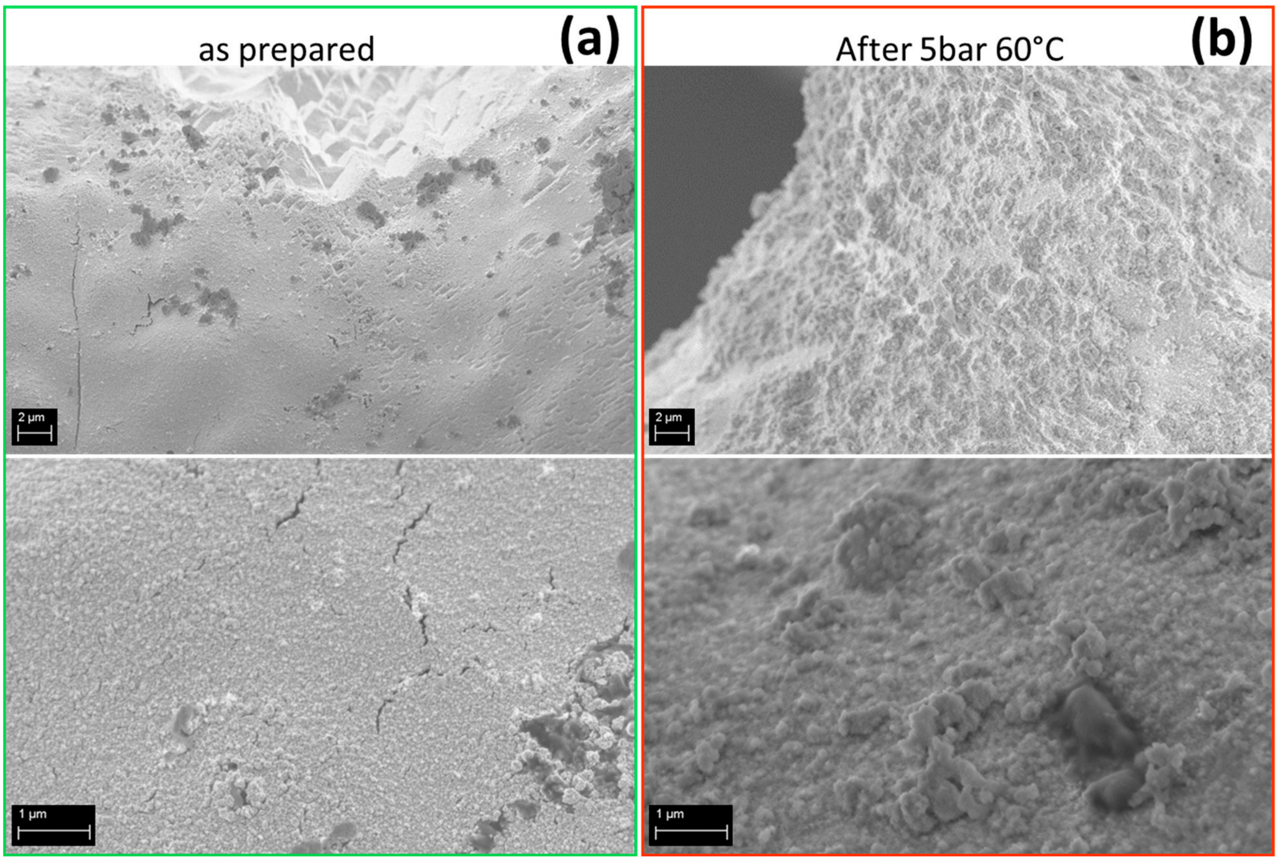

Figure S3: SEM micrographs of Au/Ni foam (a) as prepared and (b) after chronoamperometry measurements at 60°C and 5bar.

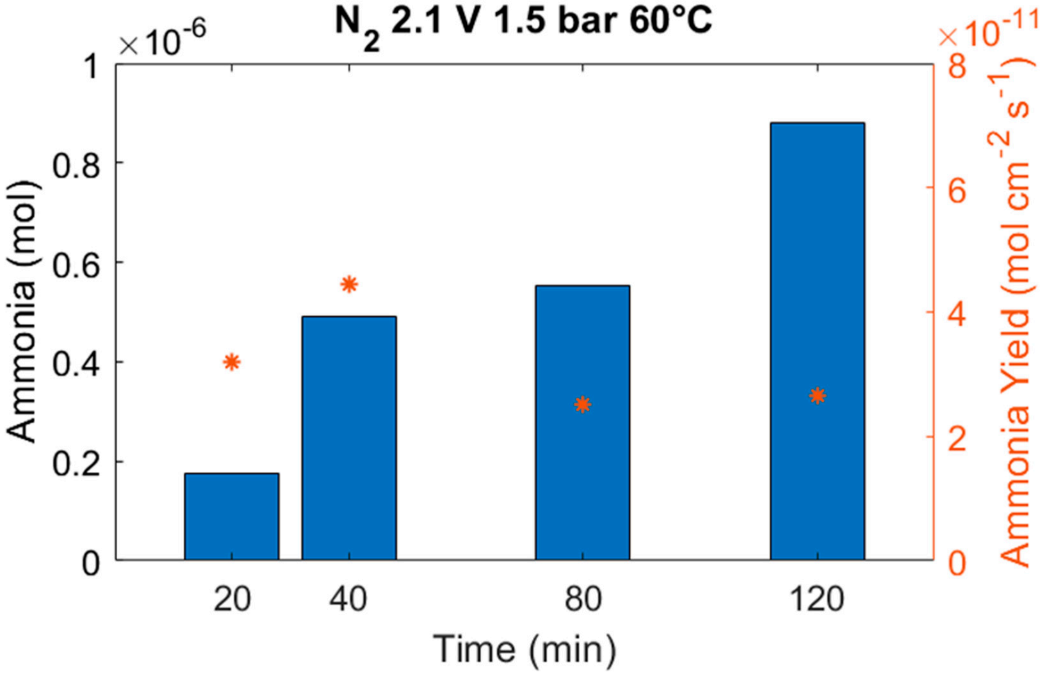

Figure S4: Ammonia moles (left axis) and yield (right axis), as a function of time of chronoamperometry, as produced by repeating four times the same experiment, with increasing time.

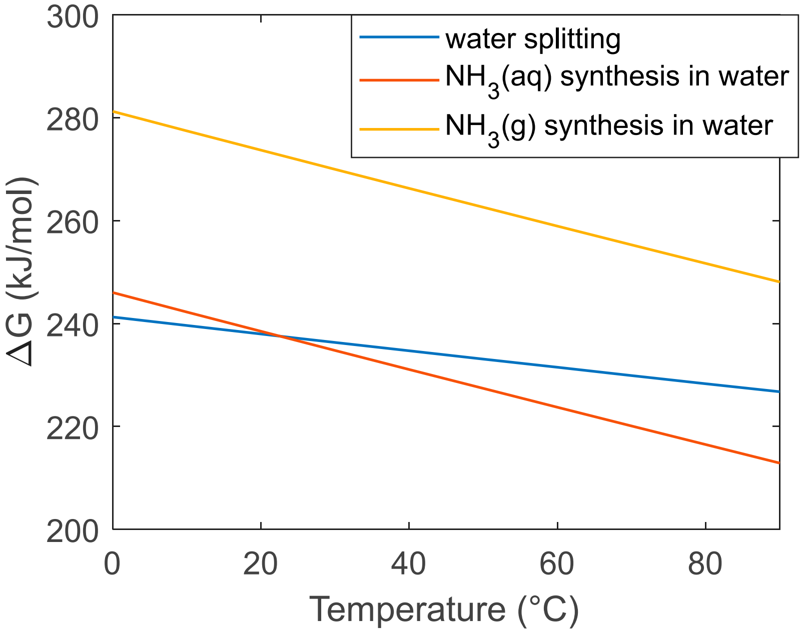

Figure S5: Gibbs free energy for water splitting, aqueous ammonia synthesis in water and gaseous ammonia synthesis in water.

Gibbs Free energy calculations

$\Delta G = \Delta H - T\Delta S$

Where H is the enthalpy and S the entropy.

Enthalpy and Entropy as a function of temperature T have been calculated according to the Shomate equation, with the values available at the NIST website https://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&Mask=2

$\Delta H_{298} = H - H°_{298.15} = A*t + B*t^2/2 + C*t^3/3 + D*t^4/4 - E/t + F - H$

$\Delta S = A*\ln(t) + B*t + C*t^2/2 + D*t^3/3 - E/(2*t^2) + G$

H° = standard enthalpy (kJ/mol)
S° = standard entropy (J/mol*K)
t = temperature (K) / 1000.

The values adopted for the involved atomic species are the following:

Liquid Water

Temperature (K)	298. - 500.
A	-203.6060
B	1523.290
C	-3196.413
D	2474.455
E	3.855326
F	-256.5478
G	-488.7163
H	-285.8304
Reference	Chase, 1998

Quantity	Value	Units	Method	Reference	Comment
$\Delta_f H°_{liquid}$	-285.830 ± 0.040	kJ/mol	Review	Cox, Wagman, et al., 1984	CODATA Review value
$\Delta_f H°_{liquid}$	-285.83	kJ/mol	Review	Chase, 1998	Data last reviewed in March, 1979
Quantity	**Value**	**Units**	**Method**	**Reference**	**Comment**
$S°_{liquid}$	69.95 ± 0.03	J/mol*K	Review	Cox, Wagman, et al., 1984	CODATA Review value
Quantity	**Value**	**Units**	**Method**	**Reference**	**Comment**
$S°_{liquid,1\ bar}$	69.95	J/mol*K	Review	Chase, 1998	Data last reviewed in March, 1979

$(\Delta H_T)_{H2O} = \Delta_f H^0_{liquid} + \Delta H_{298}$

For the water splitting reaction $(\Delta H_T)_{ws} = (\Delta H_T)_{H2} + 0.5\ (\Delta H_T)_{O2} - (\Delta H_T)_{H2O}$

The same expression can be developed for the entropy, to obtain the Gibbs free energy for water electrolysis, as reported in Fig. S2.

Hydrogen (gas)

Temperature (K)	298. - 1000.
A	33.066178
B	-11.363417
C	11.432816
D	-2.772874
E	-0.158558
F	-9.980797
G	172.707974
H	0.0
Reference	Chase, 1998
Comment	Data last reviewed in March, 1977; New parameter fit October 2001

Quantity	Value	Units	Method	Reference	Comment
$S°_{gas,1 bar}$	130.680 ± 0.003	J/mol*K	Review	Cox, Wagman, et al., 1984	CODATA Review value
$S°_{gas,1 bar}$	130.68	J/mol*K	Review	Chase, 1998	Data last reviewed in March, 1977

Oxygen (gas)

Temperature (K)	100. - 700.
A	31.32234
B	-20.23531
C	57.86644
D	-36.50624
E	-0.007374
F	-8.903471
G	246.7945
H	0.0
Reference	Chase, 1998
Comment	Data last reviewed in March, 1977; New parameter fit January 2009

Quantity	Value	Units	Method	Reference	Comment
$S°_{gas,1 bar}$	205.152 ± 0.005	J/mol*K	Review	Cox, Wagman, et al., 1984	CODATA Review value
$S°_{gas,1 bar}$	205.15	J/mol*K	Review	Chase, 1998	Data last reviewed in March, 1977

Nitrogen (gas)

Temperature (K)	100. - 500.
A	28.98641
B	1.853978
C	-9.647459
D	16.63537
E	0.000117
F	-8.671914
G	226.4168
H	0.0
Reference	Chase, 1998
Comment	Data last reviewed in March, 1977; New parameter fit January 2009

Quantity	Value	Units	Method	Reference	Comment
$S^{\circ}_{gas,1\ bar}$	191.609 ± 0.004	J/mol*K	Review	Cox, Wagman, et al., 1984	CODATA Review value
$S^{\circ}_{gas,1\ bar}$	191.61	J/mol*K	Review	Chase, 1998	Data last reviewed in March, 1977

Ammonia (gas)

Temperature (K)	298. - 1400.
A	19.99563
B	49.77119
C	-15.37599
D	1.921168
E	0.189174
F	-53.30667
G	203.8591
H	-45.89806
Reference	Chase, 1998
Comment	Data last reviewed in June, 1977

Quantity	Value	Units	Method	Reference	Comment
$\Delta_f H^{\circ}_{gas}$	-45.94 ± 0.35	kJ/mol	Review	Cox, Wagman, et al., 1984	CODATA Review value
$\Delta_f H^{\circ}_{gas}$	-45.90	kJ/mol	Review	Chase, 1998	Data last reviewed in June, 1977
Quantity	Value	Units	Method	Reference	Comment
$S^{\circ}_{gas,1\ bar}$	192.77 ± 0.05	J/mol*K	Review	Cox, Wagman, et al., 1984	CODATA Review value
$S^{\circ}_{gas,1\ bar}$	192.77	J/mol*K	Review	Chase, 1998	Data last reviewed in June, 1977

$(\Delta H_T)_{NH3} = \Delta_f H^0_{gas} + \Delta H_{298}$

For ammonia synthesis in water $(\Delta H_T)_{NH3} = (\Delta H_T)_{NH3} + 3/4\ (\Delta H_T)_{O2} - 3/2(\Delta H_T)_{H2O} - 0.5(\Delta H_T)_{N2}$