Electronic Supplementary Information (ESI)

Strategies in Cell Design and Operation for the Electrosynthesis of Ammonia: Status and Prospects

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List of figures:

Glossary of terms:

r_m	mass-specific NH_3 production rate	EDA	ethylenediamine
r_{geo}	geometric-surface-area-specific NH_3 production rate	GC-MS	gas chromatography-mass spectrometry
FE	faradaic efficiency	CEM	cation exchange membrane
E	potential	G	graphene
j_{NH_3}	current density toward NH_3 production	rGO	reduced graphene oxide
NMR	nuclear magnetic resonance	AEM	anion exchange membrane
CP	carbon paper	ZIF	zeolitic imidazolate framework
N/A	not available	HHTP	hexahydroxytriphenylene
RHE	reversible hydrogen electrode	MOF	metal-organic framework
ISE	ion-selective electrode	PEBCD	poly(N-ethyl-benzene-1,2,4,5-tetracarboxylic diimide)
IB	indophenol blue	CNT	carbon nanotube
CC	carbon cloth	PBS	phosphate buffer solution
IC	ion chromatography	Cys	cysteine

Table S1: Summary of Previous Aqueous ENRR Studies Performed in Non-separated (NS) Cells.

Catalyst	Substrate	Electrolyte	r_m ($\mu g\ h^{-1}\ mg_{cat}^{-1}$)	r_{geo} ($\times 10^{-10}$ mol $s^{-1}\ cm_{geo}^{-2}$)	*FE* (%)	*E*	vs.	j_{NH_3} ($mA\ cm^{-2}$)	NH_3 detection method	Qualitative or quantitative NMR available?	Test duration (h)	Ref.
RuPt@C	CP	1 M KOH	N/A	6.37	1.2	-0.077	RHE	0.184	Nessler	None	1	[1]
Au	Au foil	0.1 M KOH	N/A	0.038	0.12	-0.5	RHE	0.001	ISE	None	10	[2]
Ni@N-C	Glassy C	0.1 M KOH	106.3	13.9	11.6	-0.3	RHE	0.402	IB, Nessler	None	1	[3]
Defective C	CC	0.1 M Na_2SO_4, 0.02 M H_2SO_4	N/A	2.59	6.9	-0.3	RHE	0.075	IB	None	1	[4]
$NiGeO_4$@C	Ni foam	0.1 M KOH	3.06	N/A	3.57	-0.1	RHE	N/A	IB	None	2	[5]
Au@N-C	Membrane	0.1 M HCl	N/A	5.88	10.9	-0.2	RHE	0.170	IB, NMR	Qualitative	3	[6]
Fe_3O_4	Ti mesh	0.1 M Na_2SO_4	4.63	0.56	2.6	-0.4	RHE	0.016	IB, NMR	Qualitative	3	[7]
Au	CP	0.1 M Na_2SO_4	40.6	0.085	18.8	-0.3	RHE	0.002	IB, NMR	Qualitative	2	[8]
Cu@polyimide	CC	0.1 M KOH	2.48	2.03	6.6	-0.3	RHE	0.059	IB, IC, NMR	Qualitative	6	[9]

Table S2: Summary of Previous Aqueous ENRR Studies Performed in Liquid-Liquid (L-L) Separated Cells.

Catalyst	Substrate	Separator	Liquid electrolyte	r_m ($\mu g\ h^{-1}\ mg_{cat}^{-1}$)	r_{geo} ($\times 10^{-10}$ mol $s^{-1}\ cm_{geo}^{-2}$)	*FE* (%)	*E*	vs.	j_{NH_3} ($mA\ cm^{-2}$)	NH_3 detection method	Qualitative or quantitative NMR available?	Test duration (h)	Ref.
Au	CP	Nafion 211	0.1 M KOH	5.49	0.27	3.9	-0.2	RHE	0.008	Nessler	None	3	[10]
Ni	Ni foam	Nafion 211	0.1 M LiCl/EDA (cathode); 0.05 M H_2SO_4 (anode)	N/A	0.36	17.2	1.8	Cell voltage	0.010	GC-MS	None	1	[11]
Mo	Mo foil	Nafion 117	0.01 M H_2SO_4	N/A	0.31	0.24	-0.49	RHE	0.009	IB	None	3	[12]
Au@TiO_2	CP	Nafion 211	0.1 M HCl	21.4	1.75	8.1	-0.2	RHE	0.051	IB	None	2	[13]
Au@CeO_x-rGO	CP	Nafion 117	0.1 M HCl	8.3	0.27	10.1	-0.2	RHE	0.008	IB	None	2	[14]
BiNi	CP	Nafion 115	0.1 M Na_2SO_4	17.38	1.42	13.7	-0.6	RHE	0.041	IB	None	2	[15]
CoP	CP	Nafion 117	1 M KOH	21.56	1.76	0.03	-0.4	RHE	0.051	IB	None	2	[16]
MnO	Ti mesh	Nafion 117	0.1 M Na_2SO_4	7.92	1.11	8.0	-0.39	RHE	0.032	IB, IC	None	3	[17]
VO_2	CP	Nafion 211	0.1 M Na_2SO_4	14.85	0.49	4.0	-0.7	RHE	0.014	IB	None	2.22	[18]
MoS_2	CP	Nafion	0.1 M Na_2SO_4	N/A	1.29	22.2	-0.25	RHE	0.037	IB	None	2	[19]
Rh	CP	Nafion 211	0.1 M KOH	23.88	1.25	0.22	-0.2	RHE	0.036	IB	None	2	[20]
Ag	CP	CEM	0.1 M HCl	N/A	0.46	4.8	-0.6	RHE	0.013	IB	None	2	[21]
B-C	Glassy C	Nafion 117	0.25 M $LiClO_4$	33.8	N/A	39.2	-0.7	RHE	N/A	IB	None	3	[22]
BiTeI	Glassy C	Nafion 211	0.1 M KOH	N/A	0.17	1.7	-0.5	Ag/AgCl	0.005	IB	None	N/A	[23]
Mo_2C@N-C	CP	Nafion 211	0.1 M Na_2SO_4	1.20	0.16	12.3	-0.2	RHE	0.005	IB	None	2	[24]
Au@N-C	CP	CEM	0.1 M HCl	3.87	0.38	12.3	-0.2	RHE	0.011	IB	None	2	[25]
Au	ITO	Nafion	0.5 M $LiClO_4$	N/A	0.61	35.9	-0.4	RHE	0.018	Nessler	None	12	[26]
PdCu@G	CP	Nafion 117	0.1 M KOH	2.8	N/A	0.8	-0.2	RHE	N/A	IB	None	2	[27]
VN	CC	Nafion	0.1 M HCl	9.55	2.48	3.6	-0.3	RHE	0.072	IB	None	3	[28]
Au@C	CC	Nafion 211	0.1 M KOH	1.46	N/A	6.5	-0.25	RHE	N/A	IB	None	2	[29]
WO_3	CP	Nafion 117	0.1 M HCl	4.2	0.69	6.8	-0.12	RHE	0.020	IB	None	1	[30]
Mo_2N	Glassy C	Nafion 211	0.1 M HCl	78.4	4.53	4.5	-0.3	RHE	0.131	IB	None	3	[31]
WO_3	CP	Nafion 117	0.1 M HCl	17.28	0.28	7	-0.3	RHE	0.008	IB	None	2	[32]
WP_2	CC	Nafion 211	0.1 M KOH	N/A	1.17	7.2	-0.2	RHE	0.034	Nessler, IB, IC	None	3	[33]
Fe/Fe_3O_4	Fe foil	Nafion 115	0.1 M PBS	0.19	0.031	8.3	-0.3	RHE	0.001	IB	None	1	[34]
SnO_2	CC	Nafion	0.1 M Na_2SO_4	4.00	1.47	2.2	-0.7	RHE	0.043	IB	None	2	[35]
Mn_3O_4	CP	Nafion 211	0.1 M Na_2SO_4	11.6	0.38	3	-0.8	RHE	0.011	IB	None	2	[36]
TiO_2	Ti plate	Nafion 211	0.1 M Na_2SO_4	N/A	0.92	2.5	-0.7	RHE	0.027	IB	None	3	[37]
TiO_2@rGO	CP	FKB-PK-130 (CEM)	0.1 M Na_2SO_4	15.13	0.99	3.3	-0.9	RHE	0.029	IB	None	2	[38]
Cr_2O_3	CP	Nafion	0.1 M Na_2SO_4	25.3	0.50	6.8	-0.9	RHE	0.014	IB	None	2	[39]
Cr_2O_3	CP	Nafion 115	0.1 M HCl	28.13	0.46	8.6	-0.75	RHE	0.013	IB	None	2	[40]
$Bi_4V_2O_{11}$@CeO_2	CP	CEM	0.1 M HCl	23.21	7.58	10.2	-0.2	RHE	0.220	IB	None	2	[41]

Table S2: continued

Catalyst	Substrate	Separator	Liquid electrolyte	r_m (μg h^{-1} mg_{cat}^{-1})	r_{geo} (x 10^{-10} mol s^{-1} cm_{geo}^{-2})	*FE* (%)	*E*	vs.	j_{NH_3} (mA cm^{-2})	NH_3 detection method	Qualitative or Quantitative NMR available?	Test duration (h)	Ref.
Y_2O_3	CP	FAB-PK-130 (AEM)	0.1 M Na_2SO_4	14.2	1.06	2.5	-0.9	RHE	0.031	IB	None	2	[42]
Au@C	CC	N/A	1 M KOH	8.07	2.11	0.2	-0.5	RHE	0.061	IB	None	2	[43]
MoS_2	CC	Nafion 211	0.1 M Na_2SO_4	N/A	0.81	1.17	-0.5	RHE	0.023	IB	None	2	[44]
C_3N_4	CP	FAAM-15 (AEM)	0.1 M HCl	8.09	2.64	11.6	-0.2	RHE	0.077	IB	None	1.39	[45]
N-C	CP	Nafion 211	0.05 M H_2SO_4	23.8	2.33	1.42	-0.9	RHE	0.068	Nessler	None	2	[46]
B-G	CP	Nafion 117	0.05 M H_2SO_4	54.9	1.60	10.8	-0.5	RHE	0.046	IB, Nessler	None	2	[47]
MoP_2O_7@N/P-C	CP	Nafion 211	0.1 M KOH	18.7	N/A	9.0	-0.2	RHE	N/A	IB	None	2	[48]
Fe_2O_3	CP	Nafion 211	0.1 M Na_2SO_4	15.9	1.25	0.94	-0.8	RHE	0.036	IB	None	2	[49]
$K_3Ti_8O_{17}$	CP	Nafion 211	0.1 M HCl	31.6	0.52	15	-0.5	RHE	0.015	IB	None	2	[50]
Au	CP	CEM	0.1 M HCl	25.6	2.51	6.1	-0.2	RHE	0.073	IB	None	2	[51]
MoS_2	Glassy C	Nafion 211	0.1 M Na_2SO_4	N/A	2.9	4.6	-0.4	RHE	0.084	IB	None	2	[52]
FeOOH@G	CP	Nafion 211	0.1 M $LiClO_4$	27.3	0.45	14.6	-0.4	RHE	0.013	IB, IC	None	2	[53]
Au@Bi_2Te_3	CP	Nafion 115	0.1 M Na_2SO_4	32.7	1.07	20.4	-0.4	RHE	0.031	IB	None	2	[54]
Bi_2O_3@G	C	Nafion 117	0.1 M Na_2SO_4	5.68	0.69	11.2	-0.5	RHE	0.020	Nessler, ISE	None	2	[55]
Co@N-C	CP	Nafion 115	0.1 M Na_2SO_4	19.2	1.57	21.8	-0.9	Ag/AgCl	0.045	IB	None	3	[56]
PdRu	CP	Nafion 211	0.1 M KOH	37.2	3.67	1.85	-0.2	RHE	0.106	IB	None	2	[57]
PdRu	CP	Nafion 211	0.1 M HCl	34.2	3.41	2.4	-0.2	RHE	0.099	IB	None	2	[58]
Fe_2O_3	CC	Nafion 211	0.1 M Na_2SO_4	13.6	1.11	7.7	-0.4	RHE	0.032	IB	None	2	[59]
Y_2O_3-Zr	CP	Nafion 117	0.1 M Na_2SO_4	10.8	0.18	12.3	-0.5	RHE	0.005	IB	None	2	[60]
$PdH_{0.43}$	CP	Nafion 211	0.1 M Na_2SO_4	17.5	N/A	18.8	-0.2	RHE	N/A	IB	None	2	[61]
Au	CP	Nafion 117	1 M KOH	20	0.42	10.2	-0.2	RHE	0.012	IB, Nessler	None	3	[62]
V@Fe_2O_3	CP	Nafion 115	0.1 M HCl	68.7	1.12	5.7	-0.2	RHE	0.032	IB	None	2	[63]
Ag@TiO_2	CP	Nafion 117	0.1 M HCl	N/A	3.16	0.13	-0.6	RHE	0.091	IB	None	2	[64]
MoS_2@ZIF	CP	Nafion 117	0.1 M Na_2SO_4	56.7	4.63	30.9	-0.2	RHE	0.134	IB	None	2	[65]
Fe_3C@C	RDE	Nafion 211	0.05 M H_2SO_4	8.53	2.09	9.2	-0.2	RHE	N/A	IB	None	2	[66]
La_2O_3	CP	Nafion	0.1 M Na_2SO_4	17.0	0.22	4.8	-0.8	RHE	0.006	IB	None	2	[67]
FeS@MoS_2	CC	Nafion 211	0.1 M Na_2SO_4	6.34	1.38	3.0	-0.5	RHE	0.040	IB	None	2	[68]
MoS_2@rGO	CC	CEM	0.1 M Na_2SO_4	8.65	1.13	27.9	-0.35	RHE	0.033	IB	None	1	[69]
Mo_3Fe_3C	CP	Nafion 117	0.1 M Li_2SO4	1.23	0.16	27	-0.05	RHE	0.005	IB	None	2	[70]
Co_3HHTP_2	CP	Nafion 211	0.5 M $LiClO_4$	22.1	0.36	3.3	-0.4	RHE	0.010	IB	None	2	[71]
MoFe@P-C	FTO	Nafion 211	0.1 M HCl	34.2	0.56	16.8	-0.5	RHE	0.016	IB	None	1	[72]
AuCuB	CP	CEM	0.1 M Na_2SO_4	13.2	0.86	12.8	-0.5	RHE	0.025	IB	None	2	[73]
Pd-Ag-S	CP	Nafion 211	0.1 M Na_2SO_4	9.73	0.64	18.4	-0.2	RHE	0.018	IB	None	2	[74]

Table S2: continued

Catalyst	Substrate	Separator	Liquid electrolyte	r_m ($\mu g\ h^{-1}\ mg_{cat}^{-1}$)	r_{geo} ($\times 10^{-10}$ mol $s^{-1}\ cm_{geo}^{-2}$)	*FE* (%)	*E*	vs.	j_{NH_3} ($mA\ cm^{-2}$)	NH_3 detection method	Qualitative or Quantitative NMR available?	Test duration (h)	Ref.
$LaFeO_3$	CP	Nafion 117	0.1 M HCl	18.6	0.30	8.8	-0.55	RHE	0.009	IB, IC	None	2	[75]
NiTe@N-C	CC	Nafion	0.1 M HCl	33.3	1.63	17.4	-0.1	RHE	0.047	IB	None	2	[76]
MOF(Al)	Cu foam	Nafion 211	0.1 M KOH	10.6	N/A	22.6	0	RHE	N/A	IB, ISE	None	1	[77]
Pd	Ni foam	Nafion 117	0.1 M Na_2SO_4	13.6	5.45	20.0	-0.15	RHE	0.158	IB	None	2	[78]
Bi	CP	Nafion 117	0.1 M Na_2SO_4	13.2	0.42	10.5	-0.8	RHE	0.012	IB	None	2	[79]
Bi	CP	Nafion 117	0.1 M Na_2SO_4	23.4	0.38	19.8	-0.4	RHE	0.011	IB	None	1	[80]
PdRu	Ni foam	Nafion 211	0.1 M KOH	34.1	3.34	2.1	-0.2	RHE	0.097	IB	None	2	[81]
S-Au	Ni foam	Nafion 115	0.1 M Na_2SO_4	22.7	0.19	17.2	-0.2	RHE	0.005	IB	None	2	[82]
Pd	Ni foam	Nafion	0.1 M Na_2SO_4	18.3	N/A	10.4	-0.1	RHE	N/A	IB	None	2	[83]
S@G	CP	Nafion 211	0.5 M $LiClO_4$	28.6	0.93	7.1	-0.85	RHE	0.027	IB, IC, NMR	Qualitative	2	[84]
B	Glassy C	Nafion 211	0.05 M H_2SO_4	23.1	0.38	25.2	-0.4	RHE	0.011	IB, NMR	Qualitative	2	[85]
VS_2	CP	FKB-PK-130 (CEM)	0.1 M HCl	20.3	N/A	0.25	-0.6	RHE	0.119	IB, NMR	Qualitative	2	[86]
In_2O_{3-x}/CeO_{2-y}	CP	Nafion	0.1 M KOH	26.1	4.26	16.1	-0.3	RHE	0.123	IB, NMR	Qualitative	2	[87]
FeMo@N-C	CP	Nafion 115	0.1 M PBS	17.5	2.86	11.8	-0.25	RHE	0.083	IB, NMR	Qualitative	2	[88]
$FeMoO_4$	CC	CEM	0.5 M $LiClO_4$	45.8	1.50	7.8	-0.5	RHE	0.043	IB, NMR	Qualitative	2	[89]
$Pt@WO_3$	CP	FAB-PK-130 (AEM)	0.1 M K_2SO_4	1.62	0.13	31.1	-0.2	RHE	0.004	IB, NMR	Qualitative	2.5	[90]
Nb_2O_5	CP		0.1 M HCl	43.6	2.85	9.3	-0.55	RHE	0.082	IB, NMR	Qualitative	3	[91]
Fe@N-C	CP	FAAM-15 (AEM)	0.1 M PBS	62.9	10.3	18.6	-0.4	RHE	0.298	IB, IC, NMR	Qualitative	2	[92]
PdPb@C	CP	Nafion 211	0.1 M HCl	25.7	0.84	5.8	0.05	RHE	0.024	IB, IC, NMR	Qualitative	1	[93]
Au	CP	Nafion 117	0.1 M Li_2SO_4		1.51	73.3	-0.3	RHE	0.044	IB, IC, NMR	Qualitative	2	[94]
PEBCD	CC	Nafion 211	0.5 M $LiClO_4$ and H_2SO_4	1.57	0.33	1.7	-0.7	RHE	0.010	Nessler, NMR	Qualitative	2	[95]
Mn_3O_4@rGO	CP	Nafion 211	0.1 M Na_2SO_4	17.4	0.43	3.5	-0.85	RHE	0.012	IB, IC, NMR	Qualitative	2	[96]
Ru@CNT	Self-supporting	Glass frit	0.1 M PBS (cathode); 0.01 M H_2SO_4 (anode)	3.37	3.3	5.2	0	RHE	0.096	IB, NMR	Qualitative	2	[97]
MOF(Fe)	CP	CEM	0.1 M HCl	44.8	1.46	16.2	-0.3	RHE	0.042	IB, IC, NMR	Qualitative	2	[98]
Mo_4P_3	Self-supporting	Nafion 211	1 M PBS	N/A	2.83	4	-0.2	RHE	0.082	IB, NMR	Qualitative	2	[99]
MoN	CC	Nafion 211	0.1 M HCl	N/A	3.01	1.2	-0.3	RHE	0.087	IB, NMR	Qualitative	3	[100]
MoO_3	Glassy C	Nafion 115	0.1 M HCl	29.4	4.8	1.4	-0.4	RHE	0.139	IB, NMR	Qualitative	2	[101]
$CaCoO_x$	CP	Nafion 117	0.05 M Na_2SO_4	16.3	1.33	20.5	-0.3	RHE	0.038	IB, NMR	Qualitative	2	[102]
$B@MnO_2$	CC	Nafion 115	0.5 M $LiClO_4$	54.2	N/A	14.5	-0.4	RHE	N/A	IB, IC, NMR	Qualitative	2	[103]
S/N-C	CC	Nafion 211	0.2 M Na_2SO_4, 0.05 M H_2SO_4		9.87	8.11	-0.3	RHE	0.286	IB, NMR	Qualitative	2	[104]
Pd@C	CP	Nafion 211	0.1 M PBS	15	2.45	8.2	0.1	RHE	0.072	IB, NMR	Qualitative	3	[105]
$MoS_2@C_3N_4$	Glassy C	Nafion 211	0.1 M HCl	30.0	3.46	20.5	-0.3	RHE	0.100	IB, NMR	Qualitative	3	[106]
MoS_2	CP	Nafion 117	0.1 M Na_2SO_4	9.1	0.74	13.6	-0.3	RHE	0.022	IB, NMR	Qualitative	2	[107]

Table S2: continued

Catalyst	Substrate	Separator	Liquid electrolyte	r_m ($\mu g\ h^{-1}\ mg_{cat}^{-1}$)	r_{geo} ($\times 10^{-10}$ mol $s^{-1}\ cm_{geo}^{-2}$)	*FE* (%)	*E*	vs.	j_{NH_3} ($mA\ cm^{-2}$)	NH_3 detection method	Qualitative or Quantitative NMR available?	Test duration (h)	Ref.
$Fe@MoS_2$	Glassy C	Nafion 211	0.1 M Na_2SO_4	20.1	0.79	15.7	-0.35	RHE	0.023	IB, NMR	Qualitative	2	[108]
PdZn@N-C	CP	Nafion 117	0.1 M PBS	5.3	0.17	16.9	-0.2	RHE	0.005	IB, NMR	Qualitative	2	[109]
B_4C	CP	Nafion 115	0.1 M HCl	26.6	0.43	16	-0.75	RHE	0.013	IB, NMR	Qualitative	2	[110]
$Au@TiO_2$	CP	Nafion 117	0.01 M HCl	64.6	N/A	7	-0.4	RHE	N/A	IB, IC, NMR	Qualitative	2	[111]
Ru@N-C	CP	Nafion 117	0.1M HCl	11.0	3.59	15	-0.21	RHE	0.104	IB, NMR	Qualitative	2	[112]
$Fe_2Mo_6S_8$	Glassy C	Nafion 211	0.5 M Na_2SO_4, 0.1 M citrate buffer	70	2.29	12.5	-0.2	RHE	0.066	IB,NMR	Qualitative	2	[113]
Ti_3C_2	CP	Nafion	0.1 M KOH	0.11	0.28	7.0	-0.2	RHE	0.008	Nessler, NMR	Qualitative	3	[114]
Bi	Cu foil	Nafion 211	0.1 M HCl	5.3	0.69	10.3	-0.5	RHE	0.020	IB, IC, NMR	Qualitative	2	[115]
B	CP	CEM	0.1 M Na_2SO_4	13.2	0.22	4.0	-0.8	RHE	0.006	IB, NMR	Qualitative	2	[116]
fluorographene	CP	Nafion 117	0.1 M Na_2SO_4	9.3	0.30	4.2	-0.7	RHE	0.009	IB, IC, NMR	Qualitative	2	[117]
TiO_2	Ti mesh	Nafion 211	0.1 M HCl	N/A	1.24	9.2	-0.15	RHE	0.036	IB, IC, NMR	Qualitative	3	[118]
MoS_2	Ni foil	Nafion 211	0.25 M $LiClO_4$	N/A	10.3	27.7	-0.2	RHE	0.298	IB, NMR	Qualitative	0.67	[119]
$Mo/Mo_2C@N$-CNT	CC	CEM	5 mM H_2SO_4, 0.1 M K_2SO_4	8.1	1.32	5.9	-0.25	RHE	0.038	IB, IC, NMR	Qualitative	2	[120]
VN	Ti mesh	Nafion	0.1 M HCl	3.6	0.84	2.3	-0.5	RHE	0.024	IB, NMR	Qualitative	3	[121]
Au_{25}-Cys-Mo	CP	Nafion 117	0.1 M HCl	34.5	N/A	26.5	-0.2	RHE	0.609	Nessler, IB, NMR	Qualitative	3	[122]
$P\text{-}C_3N_4$	CP	Nafion	0.1 M Na_2SO_4	28.7	N/A	22.2	-0.3	RHE	N/A	IB, NMR	Qualitative	2	[123]
Ru@N-C	Glassy C	Nafion 211	0.05 M H_2SO_4	120.9	5.04	29.6	-0.2	RHE	0.146	IB, NMR	Qualitative	2	[124]
MoO_2-MoO_3	CP	Nafion 211	0.05 M H_2SO_4	60.9	1.99	23.8	-0.35	RHE	0.058	IB, NMR	Qualitative	2	[125]
$Al@Co_3O_4$	Ni foam	Nafion 117	0.1 M KOH	N/A	0.65	6.3	-0.2	RHE	0.019	IB, NMR	Quantitative	2	[126]
Pd-Ag-Au	ITO	Nafion 211	0.5 M $LiClO_4$	N/A	2.25	44.1	-0.4	RHE	0.065	IB, NMR	Quantitative	4	[127]
Mo_2C	CP	Nafion 115	0.1 M HCl	35.2	11.5	6.8	-0.3	RHE	0.333	IB, NMR	Quantitative	3	[128]
TiO_2	Ti plate	Nafion	0.1 M HCl	16.7	0.90	26	-0.5	RHE	0.026	IB, NMR	Quantitative	2	[129]
Pd-Ag	ITO	Nafion 211	0.5 M $LiClO_4$	N/A	7.45	19.6	-0.6	RHE	0.216	IB, NMR	Quantitative	12	[130]
Fe@N-C	Glassy C	Nafion 211	0.1 M KOH	53.1	N/A	39.6	-0.35	RHE	N/A	IB, NMR	Quantitative	2	[131]
$NbSe_2$	Ni foam	FKB-PK-130 (CEM)	0.1 M Na_2SO_4	89.5	14.6	6.8	-0.45	RHE	0.423	IB, IC, NMR	Quantitative	2	[132]
MOF(NiFe)@C	Glassy C	Nafion	0.1 M $NaHCO_3$	9.3	1.52	11.5	-0.347	RHE	0.044	Enzymatic kit, IB, NMR	Quantitative	1	[133]
$Fe_3C/Fe_2O_3/Fe@C$	CC	Nafion 115	6 M KOH	0.3	0.05	0.4	0.1	RHE	0.001	IB, IC, NMR	Quantitative	0.17	[134]
$Mo_2C@C$	CC	CEM	0.5 M Li_2SO_4	3.7	N/A	1.1	-0.3	RHE	N/A	Nessler, ISE, NMR	Quantitative	2	[135]
Pd_3Bi	Glassy C	FAB-PK-130 (AEM)	0.05 M H_2SO_4	59.1	2.32	21.5	-0.2	RHE	0.067	IB, NMR	Quantitative	2	[136]
$Mo@MnO_2$	CC	N/A	0.1 M Na_2SO_4	36.6	1.20	7.9	-0.5	RHE	0.035	IB, NMR	Quantitative	2	[137]
Pd@N-C	CP	Nafion 211	0.05 M H_2SO_4	69.2	5.65	24.8	-0.45	RHE	0.164	IB, NMR	Quantitative	2	[138]
$Ru@MoS_2$	CP	FAAM-15 (AEM)	0.01 M HCl	5.6	0.91	12.2	-0.15	RHE	0.026	IB, NMR	Quantitative	1	[139]

Table S2: continued

Catalyst	Substrate	Separator	Liquid electrolyte	r_m (μg h^{-1} mg_{cat}^{-1})	r_{geo} (x 10^{-10} mol s^{-1} cm_{geo}^{-2})	*FE* (%)	*E*	vs.	j_{NH_3} (mA cm^{-2})	NH_3 detection method	Qualitative or Quantitative NMR available?	Test duration (h)	Ref.
Au	ITO	Nafion 211	0.5 M $LiClO_4$	N/A	0.65	14.8	-0.5	RHE	0.019	Nessler, NMR	Quantitative	2	[140]
Au@$MoSe_2$	CP	Nafion 117	0.1 M Na_2SO_4	30.8	1.01	37.8	-0.3	RHE	0.029	IB, NMR	Quantitative	2	[141]
VN@N/S-C	CP	Nafion 211	0.1 M HCl	20.5	N/A	8.6	-0.3	RHE	N/A	IB, NMR	Quantitative	2	[142]
Fe@MoS_2	CP	Nafion 211	0.5 M K_2SO_4	8.6	1.13	18.8	-0.3	RHE	0.033	IB, NMR	Quantitative	2	[143]
Mo@N-C	CP	Glass frit	0.1 M KOH	34	5.56	14.6	-0.3	RHE	0.161	Nessler, NMR	Quantitative	1	[144]
Bi@C	CP	CEM	1.0 M K_2SO_4	3400	144.4	66	-0.5	RHE	4.181	Nessler, NMR	Quantitative	2	[145]
Bi_5O_7I@C	Ti plate	Nafion 211	0.1 M Na_2SO_4, 2.25 mg_{cat} mL^{-1}	113.9	1.40	6.4	-0.4	RHE	0.040	IB, IC, NMR	Quantitative	2	[146]

Table S3: Summary of Previous Aqueous ENRR Studies Performed in Gas-Liquid (G-L) Separated Cells.

Catalyst	Substrate	Separator	Liquid electrolyte in the anode compartment	r_m (μg h^{-1} mg_{cat}^{-1})	r_{geo} (x 10^{-10} mol s^{-1} cm_{geo}^{-2})	*FE* (%)	*E*	vs.	j_{NH_3} (mA cm^{-2})	NH_3 detection method	Qualitative or Quantitative NMR available?	Test duration (h)	Ref.
Ru	C felt	Nafion	2 M KOH	N/A	0.034	0.28	-1.1	Ag/AgCl	0.001	IB, IC	None	24	[147]
Pt@C	CP	Nafion 211	0.1 M Li_2SO_4	41.6	1.4	0.07	2	Cell voltage	0.039	ISE, Nessler	None	1	[148]
Fe_2O_3@CNT	CP	Nafion 115	$KHCO_3$	0.22	0.036	0.03	-2	Ag/AgCl	0.001	IB, ISE	None	6	[149]
Fe_2O_3@CNT	CP	Nafion 115	0.5 M KOH	0.26	0.11	0.16	-2	Ag/AgCl	0.003	IB	None	4	[150]
Fe_2O_3	CP	FAA-3 (AEM)	0.5 M KOH	0.95	0.16	0.04	1.6	Cell voltage	0.005	IB, Nessler	None	1	[151]
Fe_2O_3@CNT	CP	Nafion 115	0.1 M KOH	0.14	0.075	6.0	-0.9	Ag/AgCl	0.002	Nessler	None	4	[152]
$CrO_{0.66}N_{0.56}$	Membrane	Nafion 117	H_2O	11.8	0.68	6.7	1.8	Cell voltage	0.020	ISE	None	1	[153]
Fe_2O_3@CNT	CP	Nafion 115	0.5 M KOH	41.4	0.34	17	-0.5	RHE	0.010	IB, ISE	None	2	[154]
Fe_2O_3@CNT	CP	Nafion 115	0.5 M KOH	24.1	N/A	3.4	-0.5	RHE	N/A	IB	None	2	[155]
Ag@N-C	CP	Nafion 117	0.1 M HCl	270.9	8.9	19.5	-0.6	RHE	0.256	IB, IC, NMR	Qualitative	2	[156]
Cu	CP	Exellion (AEM)	0.32 M KOH	N/A	8.6	6.3	-0.5	RHE	0.249	Nessler, NMR	Quantitative	1	[157]

Table S4: Summary of Previous Aqueous ENRR Studies Performed in Gas-Gas (G-G) Separated Cells.

Catalyst	Substrate	Separator	Liquid electrolyte	r_m (μg h^{-1} mg_{cat}^{-1})	r_{geo} (x 10^{-10} mol s^{-1} cm_{geo}^{-2})	*FE* (%)	*E*	vs.	j_{NH_3} (mA cm^{-2})	NH_3 detection method	Qualitative or Quantitative NMR available?	Test duration (h)	Ref.
Ru	Membrane	Nafion 417	N/A	N/A	0.0049	0.0015	N/A	N/A	0.0001	IB	None	N/A	[158]
$SmFe_{0.7}Cu_{0.1}Ni_{0.2}O_3$	Self-supporting	Nafion 102	N/A	N/A	113	90.4	2	Cell voltage	3.271	Nessler	None	N/A	[159]
Pt@C	CP	Nafion 211	N/A	189.7	31	2	0.2	Cell voltage	0.897	ISE	None	1	[160]
Au@C	CP	FAAM-PK-75 (AEM)	N/A	2.22	0.15	0.55	-0.4	RHE	0.004	Nessler	None	1	[161]
Pt@C	CP	Celgard 3401	6 M KOH	9.91	0.40	0.011	0.5	Cell voltage	0.012	IB	None	1.5	[162]
VN	CP	Nafion 211	N/A	40.5	3.3	6	-0.1	RHE	0.096	Nessler, elemental analysis, NMR	Qualitative	2	[163]
Pd-Ag	CP	Nafion 211	N/A	N/A	3.2	7.9	-0.07	RHE	0.092	IB, NMR	Quantitative	6	[130]

Table S5: Detailed Comparison of Experimental Procedures in Conducting Quantitative Isotope NMR Tests for the Aqueous ENRR.

Ref.	$^{15}N_2$ purity (atom %)	Gas cleaning traps (in the listed order)	Repetition on quantitative NMR experiments	Cross-examination with colorimetric NH_3 measurements		
				$^{15}NH_3$ by NMR	$^{14}NH_3$ by NMR	$^{14}NH_3$ by colorimetric methods (IB or Nessler)
126	N/A	Alkaline, acid	N/A	6.54 x 10^{-11} mol s^{-1} cm_{geo}^{-2}	6.67 x 10^{-11} mol s^{-1} cm_{geo}^{-2}	6.48 x 10^{-11} mol s^{-1} cm_{geo}^{-2}
127	98	Acid, H_2O	N/A	71.9 μM	N/A	78.4 μM
128	N/A	N/A	N/A	94.8 μg h^{-1} mg_{cat}^{-1}	N/A	95.1 μg h^{-1} mg_{cat}^{-1}
129	98	Acid, H_2O	N/A	14.25 – 14.94 μM	16.2 – 17.01 μM	15.90 μM
130	98	Acid	N/A	769.3 μM	706.7 μM	804.9±65.3 μM
131	98	N/A	N/A	51.86 μg h^{-1} mg_{cat}^{-1}	52.09 μg h^{-1} mg_{cat}^{-1}	53.12 μg h^{-1} mg_{cat}^{-1}
132	N/A	Alkaline, $FeSO_4$, acid	N/A	260.9 μM	N/A	264.4 μM
133	N/A	Acid	N/A	9.0 μg h^{-1} mg_{cat}^{-1}	N/A	9.3 μg h^{-1} mg_{cat}^{-1}
134	98	N/A	N/A	124 ppb	N/A	165 ppb
135	99	N/A	N/A	4.2 μg h^{-1} mg_{cat}^{-1}		11.3 μg h^{-1} mg_{cat}^{-1}
136	99	N/A	N/A	7.91 μg mL^{-1} or 59.3 μg h^{-1} mg_{cat}^{-1}	7.78 μg mL^{-1} or 58.3 μg h^{-1} mg_{cat}^{-1}	59.05±2.27 μg h^{-1} mg_{cat}^{-1}
137	N/A	Acid	Triplet measurements for the NMR spectroscopy from the same electrolyte sample	0.378 μg mL^{-1}	N/A	0.366 μg mL^{-1}
138	N/A	Alkaline, $FeSO_4$, acid	N/A	51.2 μM	50.7±1.8 μM	50.9 μM
139	98	Acid	N/A (Error bars provided)	28±3 nmol or 5.5±0.6 μM	30±3 nmol	28±3 nmol
140	N/A	N/A	N/A (Error bars provided)	N/A	N/A (below lower detection range of 100 μM)	N/A (only the normalized rate was provided: 0.65 x 10^{-10} mol s^{-1} cm_{geo}^{-2})
141	99	Alkaline, $FeSO_4$, acid	N/A (Error bars provided)	33.2±0.9 μg h^{-1} mg_{cat}^{-1}	31.0±1.1 μg h^{-1} mg_{cat}^{-1}	30.8 μg h^{-1} mg_{cat}^{-1}
142	N/A	Alkaline, acid	N/A	N/A	0.5 μg mL^{-1}	N/A
143	N/A	N/A	N/A	0.124 μg mL^{-1}	N/A	0.122 μg mL^{-1}
144	N/A	N/A	N/A	45.2 μM	N/A	46.3±1.8 μM
145	N/A	N/A	N/A	26.7 μmol	N/A	25.7 μmol
146	98	N/A	N/A	Values are claimed to be close but the exact values are not disclosed explicitly.		
157	N/A	Acid, Alkaline	N/A	The *FE* calculated from the NMR-detected $^{15}NH_3$ is 86% of that calculated from the detected NH_3 via the Nessler's reagent test.		

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