Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information

Calculation of TOF for NiP catalysts

Calculation of turn over frequencies utilised the surface areas of the catalysts determined by BET and the assumption that each Nitrogen molecule covers 0.162 nm^2. Both Ni and P sites are considered, and hence each N_2 molecule is assumed to cover two sites. The turnover numbers were calculated as follows.

Material	Density / g cm^{-3}	Molar mass / g mol^{-1}	Molar volume / cm^3 mol^{-1}	Surface site density / cm^{-3}
Ni_2P	7.35	148.36	20.19	2.00x10^{15}
$Ni_{12}P_5$	7.53	859.19	114.14	6.31x10^{14}

<u>Surface site density</u>

#atoms in 1 cm^3 = N(atoms in formula)xN_A/V_M

atoms in 1 cm^2 = ((#atoms)$^{1/3}$)^2= (#atoms)$^{2/3}$

<u>Roughness Factor of electrode</u>

$$R_f\left(\frac{cm^2}{cm^2}\right) = Loading\left(\frac{mg}{cm^2}\right) \times 0.001\left(\frac{g}{mg}\right) \times Specific\ area\left(\frac{m^2}{g}\right) \times 10000\left(\frac{cm^2}{m^2}\right)$$

<u>Specific current density</u>

$$j_{sp}\left(\frac{mA}{cm^2}\right) = j_{obs}\left(\frac{mA}{cm^2}\right)R_f\left(\frac{cm^2}{cm^2}\right)$$

<u>Specific molecular production rate</u>

For the reaction $2H^+ + 2e^- \rightarrow H_2$, n=2

$$Prod_{sp}\left(\frac{molecule}{cm^2 \cdot s}\right) = j_{sp}\left(\frac{mA}{cm^2}\right)0.001\left(\frac{A}{mA}\right)\frac{1}{Faraday}\left(\frac{1}{C \cdot mol^{-1}}\right)\frac{1}{n}(unitless)N_A\left(\frac{molecule}{mol}\right)$$

<u>Site density per specific area</u>

$$AtomsIncc\left(\frac{1}{cm^3}\right) = \frac{N(atoms\ in\ formula)N_A(mol^{-1})}{V_M(cm^3mol^{-1})}$$

$$Sites_{sp}\left(\frac{1}{cm^2}\right) = \left(AtomsIncc\left(\frac{1}{cm^3}\right)\right)^{2/3}$$

<u>Turnover frequency</u>

$$TOF\left(\frac{molecules}{s}\right) = \frac{Prod_{sp}\left(\frac{molecules}{cm^2 \cdot s}\right)}{Sites_{sp}\left(\frac{1}{cm^2}\right)}$$

Catalyst	Loading /mg cm^{-2}	SA /m^2 g^{-1}	Rf	Site density /cm^{-3}	$-j_{-0.10V,sp}$ /µA cm^{-2}	$-j_{-0.20V,sp}$ /µA cm^{-2}	$TOF_{-0.1V}$ /s^{-1}	$TOF_{-0.2V}$ /s^{-1}	Ref
$Ni_2P_{as\ recv}$	0.15	1	1.5	2.00×10^{15}	89	673	0.140	1.051	this work
$Ni_2P_{(6hr)}$	0.15	1.18	1.8	2.00×10^{15}	85	1110	0.132	1.737	this work
$Ni_2P_{(9hr)}$	0.15	1.38	2.1	2.00×10^{15}	62	1270	0.096	1.975	this work
$Ni_{12}P_5$	0.15	16.1	24.1	6.30×10^{14}	4	16	0.019	0.081	this work
Ni_2P	1.0	32.8	328	2.00×10^{15}	10	320	0.015	0.500	1
CoP[b]	0.9	59.1	532	2.45×10^{15}	48	NR	0.061	NR	2
MoS[a]	NR	NR	90	1.11×10^{15}	NR	111	NR	0.312	3

(a) loading not provided in text, but roughness factor provided in supplementary materials; NR: not reported

Bode plot of Ni_2P (6hr ball milled) as a function of the applied overpotential. Symbols: Data, line: fit. Frequency range: 100 kHz to 0.2Hz at 10 points/decade. A sinusoidal perturbation of 10 mV_{pp} was used.

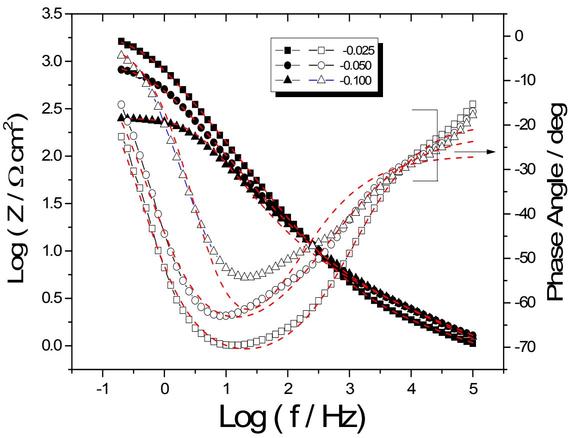

Table giving the equivalent circuit parameters derived using the 2TP model and 2TS model used respectively for Ni_2P and $Ni_{12}P_5$ based electrodes as a function of the applied overpotential. For Ni_2P based electrodes, R_s corresponds to the solution resistance associated with the electrolyte used and R_{CT}&CPE_{DL} with n_1 and R_2 &CPE_2 with n_2 represent the two time constant associated with the *her* reaction in acidic medium.

Catalyst	η / V vs. RHE	Rs / Ω	R_{ct} / Ω cm^2	R_2 /Ω cm^2	CPE_{DL} /Fcm^{-2}s^{n-1}	CPE_2 /Fcm^{-2}s^{n-1}	n_{DL}	n_2
Bulk Ni_2P	-0.1	4.5	1.51E+03	7.60E+02	2.33E-11	1.15E-05	0.89	1
	-0.15	4.5	9.09E+02	2.90E+02	2.36E-11	2.01E-05	0.7	1
	-0.2	4.5	5.06E+02	1.97E+02	2.40E-11	3.13E-05	0.83	1
	-0.25	4.5	3.36E+02	2.88E+01	2.36E-11	3.47E-05	0.82	1
	-0.3	4.5	2.17E+02	2.16E+01	2.29E-11	7.29E-05	0.81	1
	-0.35	4.5	1.52E+02	1.16E+01	2.33E-11	1.39E-04	0.8	1
	-0.4	4.5	1.28E+02	6.60E+00	2.26E-11	2.34E-04	0.8	1
6 hr ball milled Ni_2P	-0.025	4.5	3.45E+03	2.53E+03	1.24E-10	1.32E-06	0.84	0.55
	-0.05	4.5	1.67E+03	1.19E+03	1.47E-10	5.00E-06	0.86	0.35
	-0.1	4.5	4.44E+02	3.47E+02	1.27E-10	8.68E-06	0.95	0.3
	-0.2	4.5	4.69E+01	2.38E+02	1.32E-10	1.63E-05	0.9	0.27
	-0.3	4.5	1.49E+01	8.50E+01	1.47E-10	2.35E-05	0.7	0.21
	-0.4	4.5	9.03E+00	3.40E+01	1.32E-10	4.68E-05	0.66	0.14
9 hr ball milled Ni_2P	-0.1	4.5	6.57E+02	5.17E+02	1.59E-10	8.05E-06	0.87	0.3
	-0.15	4.5	2.54E+02	1.79E+02	1.43E-10	1.58E-05	0.85	0.23
	-0.2	4.5	4.57E+01	3.97E+01	1.64E-10	3.67E-05	0.71	0.18
	-0.3	4.5	1.72E+01	7.25E+00	1.61E-10	2.26E-05	0.7	0.17
	-0.35	4.5	1.43E+01	3.93E+00	1.64E-10	6.79E-05	0.63	0.03

Catalyst	η / V vs. RHE	Rs / Ω	R_1 / Ω cm^2	R_2 /Ω cm^2	CPE_1 /10^{-3} Fcm^{-2}s^{n-1}	CPE_2 /10^{-6} Fcm^{-2}s^{n-1}	n_1	n_2
$Ni_{12}P_5$ (series model)	-0.1	4.5	1.77E+04	6.25E+02	8.32E-12	5.64E-06	0.9	0.73
	-0.15	4.5	8.87E+03	2.32E+02	4.06E-12	5.70E-06	0.87	0.75
	-0.2	4.5	4.47E+03	1.16E+02	1.71E-12	5.75E-06	0.9	0.74
	-0.25	4.5	2.34E+03	4.59E+01	7.68E-13	5.72E-06	0.9	0.71
	-0.3	4.5	1.28E+03	1.93E+01	4.25E-13	5.66E-06	0.9	0.69
	-0.35	6.5	6.59E+02	9.66E+00	4.10E-13	5.78E-06	0.95	0.75
	-0.4	6.1	4.27E+02	7.25E+00	3.99E-13	5.72E-06	0.9	0.87

References

1. E. J. Popczun, J. R. McKone, C. G. Read, A. J. Biacchi, A. M. Wiltrout, N. S. Lewis and R. E. Schaak, *Journal of the American Chemical Society*, 2013, **135**, 9267-9270.
2. E. J. Popczun, C. G. Read, C. W. Roske, N. S. Lewis and R. E. Schaak, *Angew. Chem.-Int. Edit.*, 2014, **53**, 5427-5430.
3. J. D. Benck, Z. B. Chen, L. Y. Kuritzky, A. J. Forman and T. F. Jaramillo, *ACS Catalysis*, 2012, **2**, 1916-1923.