

Supporting Information (SI)

Insights into the Ni/C-Based Thin-Film Catalyst Layer Design for Urea Oxidation Reaction in a Three-Electrode System

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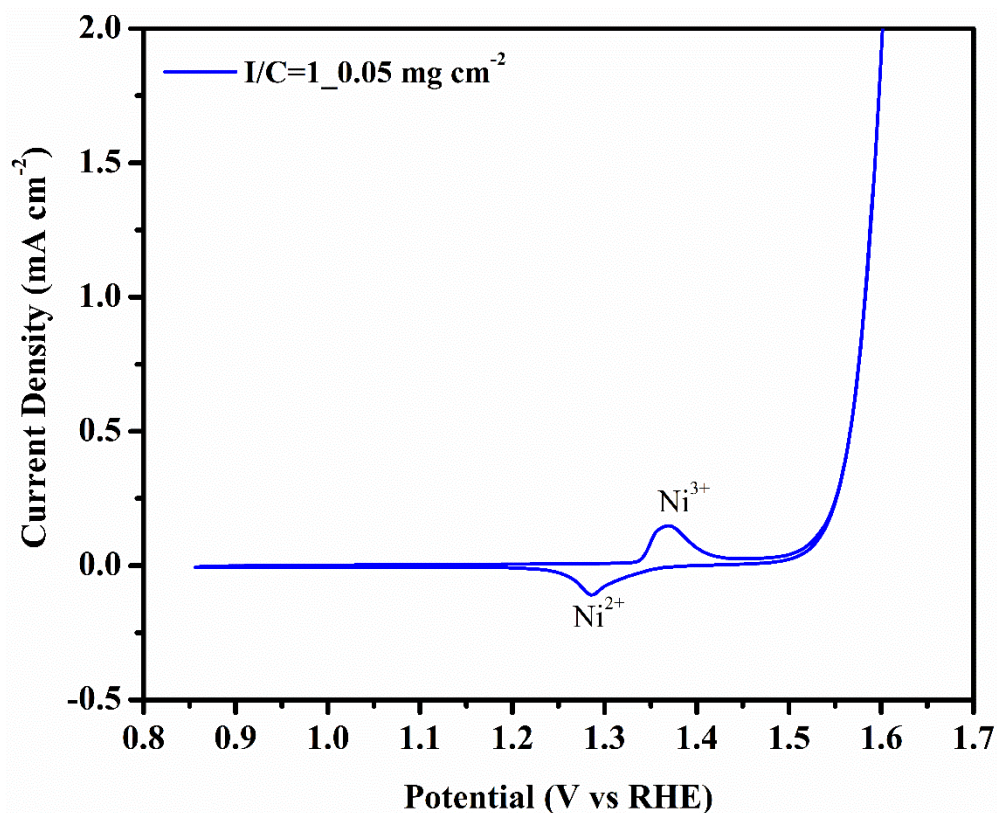


Figure S1. A sample CV curve obtained in 0.5 M KOH at a scan rate of 10 mV s^{-1} to calculate the ECSA of the catalyst layers.

The ECSA of the catalysts can be obtained by using the following formula [1]: $\text{ECSA} = Q/0.257 \cdot m$ where Q (mC) is the charge consumed during the formation of a monolayer of $\text{Ni}(\text{OH})_2$ that can be obtained from the integration of the area under the reduction peak, a charge of 0.257 mC cm^{-2} is required to reduce a monolayer of NiOOH to $\text{Ni}(\text{OH})_2$ and m (mg) is the loading amount of the catalyst.

[1] N. Kakati, J. Maiti, K.S. Lee, B. Viswanathan, Y.S. Yoon, Hollow Sodium Nickel Fluoride Nanocubes Deposited MWCNT as An Efficient Electrocatalyst for Urea Oxidation, *Electrochim. Acta.* 240 (2017) 175–185. <https://doi.org/10.1016/j.electacta.2017.04.055>.

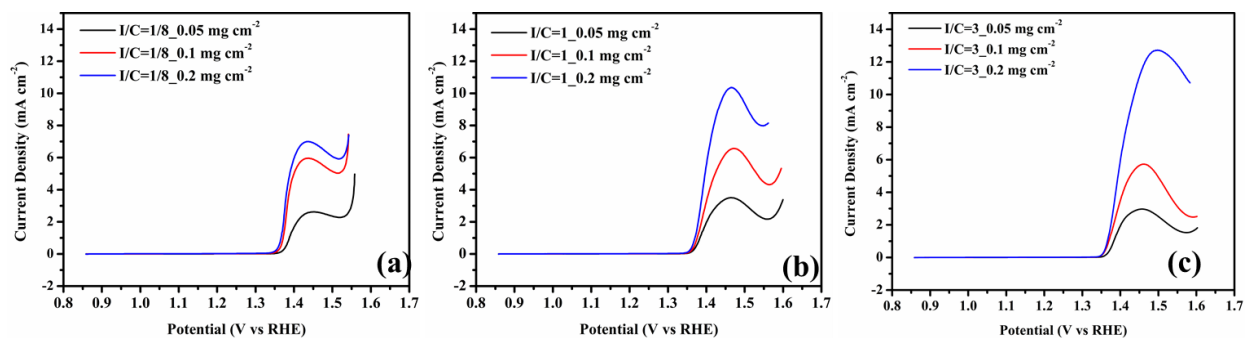


Figure S2. (a-c) LSV curves of CLs at different I/C ratio with different catalyst loading on the GCE obtained using 0.33 M urea in 0.5 M KOH at a scan rate of 10 mV s^{-1} .

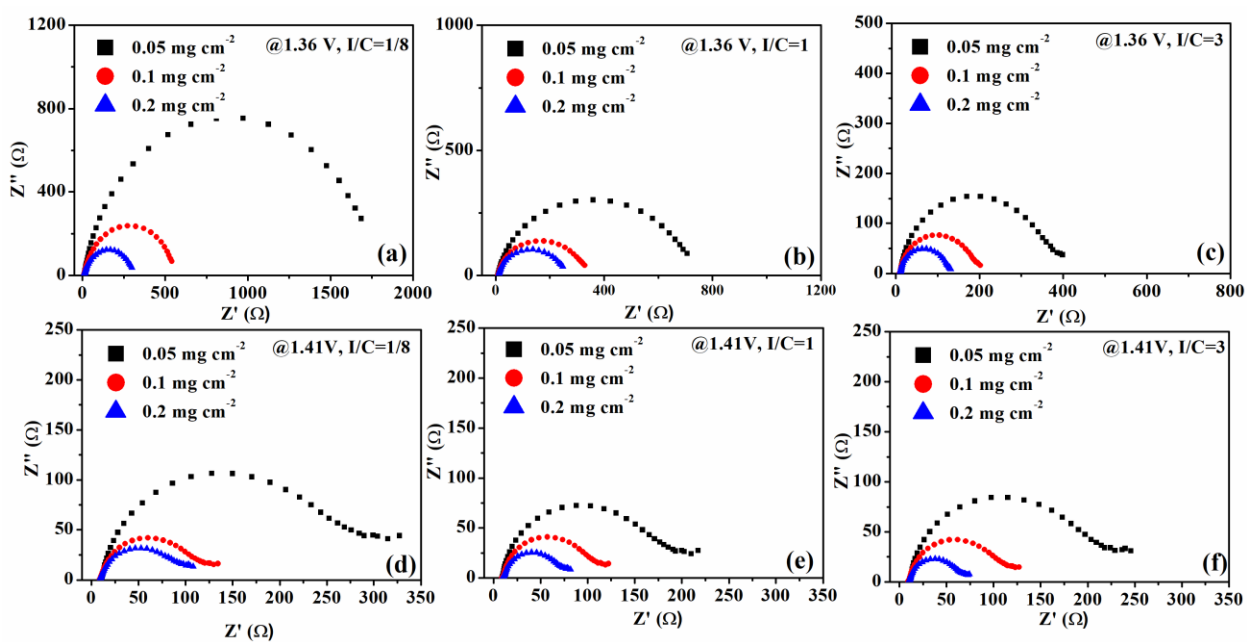
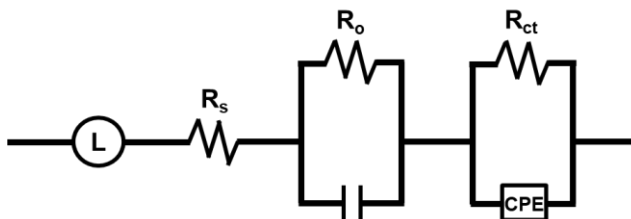


Figure S3. Electrochemical impedance spectra of the CLs at different I/C ratio with different catalyst loading on the GCE obtained using 0.33 M urea in 0.5 M KOH.

EIS Simulation



R_s is a sign of the uncompensated solution resistance, R_{ct} is a charge transfer resistance generated from urea oxidation, R_o is related to the contact resistance between the catalyst material and the glassy carbon electrode and the constant phase element (CPE) for the double layer capacitance.

Table S1 Fitted results for electrochemical impedance spectroscopy measurement for Ni/C catalyst at $I/C = 1/8$ in 0.5 M KOH electrolyte with 0.33 M Urea.

	IPA/Water=3 /1 Loading(mg cm ⁻²)	I/C=1/8, 0.33 M Urea + 0.5 M KOH						
		L (H)	R_s (Ω)	R_o (Ω)	R_{ct} (Ω)	C (F)	CPE (F s ⁻¹)	α
1.36 V	0.05	-0.832E-6 ± 0.101E-6	9.93 ± 0.027	937.2 ± 41.6	855.02 ± 40.15	0.211E-3 ± 0.012E-3	0.450E-3 ± 0.043E-3	0.772 ± 0.012
	0.1	-0.583E-6 ± 0.011E-6	8.732 ± 0.003	360.05 ± 2.45	211.5 ± 2.8	0.423E-3 ± 0.002	1.916E-3 ± 0.02E-3	0.671 ± 0.001
	0.2	-0.776E-6 ± 0.147E-6	8.758 ± 0.04	168.85 ± 9.25	148.1 ± 8.7	0.731E-3 ± 0.051E-3	2.815E-3 ± 0.405E-3	0.645 ± 0.02
1.41 V	0.05	-0.776E-6 ± 0.117E-6	10.05 ± 0.15	114.34 ± 52.06	216.05 ± 44.65	0.71E-2 ± 0.70E-2	1.40E-3 ± 1.18E-3	0.752 ± 0.129
	0.1	-0.642E-6 ± 0.101E-6	8.837 ± 0.142	42.49 ± 20.54	89.83 ± 17.27	0.0232 ± 0.02	3.17E-3 ± 2.6E-3	0.712 ± 0.138
	0.2	-0.633E-6 ± 0.075	8.812 ± 0.105	28.53 ± 10.11	77.49 ± 8.44	0.027 ± 0.02	2.86E-3 ± 2E-3	0.708 ± 0.103

Table S2 Fitted results for electrochemical impedance spectroscopy measurement for Ni/C catalyst at I/C = 1 in 0.5 M KOH electrolyte with 0.33 M Urea.

	IPA/Water= 3/1 Loading(mg cm ⁻²)	I/C=1, 0.33 M Urea + 0.5 M KOH						
		L (H)	R _s (Ω)	R _o (Ω)	R _{ct} (Ω)	C (F)	CPE (F s ⁻¹)	α
1.36 V	0.05	-0.661E-6 ± 0.005E-6	9.115 ± 0.001	408.15 ± 2.85	318.2 ± 1	0.340E-3 ± 0.004	1.082E-3 ± 0.027E-3	0.755 ± 0.003
	0.1	-0.593E-6 ± 0.003	9.16 ± 0.0015	253.2 ± 0.5	123.35 ± 7.25	0.535E-3 ± 0.016E-3	0.0115 ± 0.0005E-3	0.523 ± 0.008
	0.2	-0.378E-6 ± 0.124E-6	9.346 ± 0.003	184.95 ± 0.75	102.3 ± 0.8	0.901E-3 ± 0.002E-3	0.0137 ± 0.0002E-3	0.486 ± 0.002
1.41 V	0.05	-0.34E-6 ± 0.29E-6	9.09 ± 0.008	120.65 ± 0.15	100.05 ± 0.55	0.242E-3 ± 0.0005E-3	4.84E-3 ± 0.05E-3	0.628 ± 0.002
	0.1	-0.5E-6 ± 0.078E-6	9.09 ± 0.0345	72.39 ± 2.69	59.4 ± 3.1	0.517E-3 ± 0.012E-3	0.015 ± 0.003E-3	0.479 ± 0.025
	0.2	-0.42E-6 ± 0.07E-6	9.29 ± 0.044	40.21 ± 0.21	42.7 ± 0.73	4.63E-3 ± 4.6E-3	0.0145 ± 0.0005E-3	0.491 ± 0.007

Table S3 Fitted results for electrochemical impedance spectroscopy measurement for Ni/C catalyst at I/C = 3 in 0.5 M KOH electrolyte with 0.33 M Urea.

	IPA/Wate r=3/1 Loading(mg cm ⁻²)	I/C=3, 0.33 M Urea + 0.5 M KOH						
		L (H)	R _s (Ω)	R _o (Ω)	R _{ct} (Ω)	C (F)	CPE (F s ⁻¹)	α
1.36 V	0.05	-0.8276E-6 ± 0.094	10.34 ± 0.04	285.5 ± 4	141.9 ± 8.4	0.23E-3 ± 0.003 E-3	6.2 E-3 ± 0.91E-3	0.568 ± 0.022
	0.1	-0.4065E-6 ± 0.375	9.33 ± 0.044	145.95 ± 1.45	79.5 ± 5.03	0.471E-3 ± 0.005E-3	0.017 ± 0.003	0.467 ± 0.02
	0.2	-1.106E-6 ± 0.474E-6	9.58 ± 0.163	86.38 ± 7.12	43.4 ± 1.24	0.782E-3 ± 0.08E-3	0.02 ± 0.009	0.540 ± 0.11
1.41 V	0.05	-1.075E-6 ± 0.176E-6	10.34 ± 0.01	145 ± 0.7	116.95 ± 3.15	0.221E-3 ± 0.001E-3	5.21E-3 ± 0.24	0.591 ± 0.007
	0.1	0.523E-6 ± 0.26E-6	9.361 ± 0.028	73.17 ± 0.76	69.65 ± 2.36	0.459E-3 ± 0.0025E-3	0.014 ± 0.002	0.5 ± 0.01
	0.2	0.056E-6 ± 0.08 E-6	9.47 ± 0.049	37.38 ± 1.14	37.51 ± 1.74	0.76E-3 ± 0.018E-3	0.017 ± 0.003	0.484 ± 0.03

Table S4 Fitted results for electrochemical impedance spectroscopy measurement for Ni/C catalyst at I/C = 1 in 1.0 M KOH electrolyte with 0.33 M Urea.

	IPA/Water= 3/1 Loading(mg cm ⁻²)	I/C=1, 0.33 M Urea + 1 M KOH						
		L (H)	R _s (Ω)	R _o (Ω)	R _{ct} (Ω)	C (F)	CPE (F s ⁻¹)	α
1.36 V	0.05	-0.197E-6 ± 0.187E-6	5.741 ± 0.007	294.55 ± 4.35	212.45 ± 2.95	0.343E-3 ± 0.014E-3	0.911E-3 ± 0.074E-3	0.778 ± 0.009
	0.1	-0.389E-6 ± 0.0345E-6	5.631 ± 0.078	212 ± 30	107.5 ± 10.5	0.482E-3 ± 0.07E-3	7.7E-3 ± 5.3E-3	0.657 ± 0.114
	0.2	-0.417E-6 ± 0.003E-6	5.80 ± 0.002	135.1 ± 0.4	56.81 ± 0.34	0.929E-3 ± 0.004E-3	8.07E-3 ± 0.15E-3	0.637 ± 0.003
1.41 V	0.05	-0.425E-6 ± 0.051E-6	5.75 ± 0.006	94.89 ± 4.64	73.09 ± 3.09	0.244E-3 ± 0.01E-3	4.265E-3 ± 1.085E-3	0.669 ± 0.027
	0.1	0.406E-6 ± 0.026E-6	5.67 ± 0.02	50.305 ± 4.26	39.19 ± 1.15	0.455E-3 ± 0.431 ± 0.480 ± 0.025E-3	8.48E-3 ± 3.52E-3	0.67 ± 0.052
	0.2	-0.373E-6 ± 0.02E-6	5.80 ± 0.023	27.16 ± 0.635	25.135 ± 1.175	0.958E-3 ± 0.014E-3	0.023 ± 0.004	0.525 ± 0.026

Table S5 Fitted results for electrochemical impedance spectroscopy measurement for Ni/C catalyst at I/C = 1 in 3.0 M KOH electrolyte with 0.33 M Urea.

	IPA/Water= 3/1 Loading(mg cm ⁻²)	I/C=1, 0.33 M Urea + 3M KOH						
		L (H)	R _s (Ω)	R _o (Ω)	R _{ct} (Ω)	C (F)	CPE (F s ⁻¹)	α
1.36 V	0.05	-0.15E-4 ± 0.005E-4	3.219 ± 0.007	56.15 ± 1.28	60.05 ± 1.11	0.337E-3 ± 0.01E-3	1.29E-3 ± 0.07E-3	0.747 ± 0.006
	0.1	-0.135E-4 ± 0.002E-4	3.193 ± 0.023	43.11 ± 1.37	30.2 ± 0.55	0.473E-3 ± 0.013E-3	9.5E-3 ± 1.5E-3	0.577 ± 0.023
	0.2	-0.154E-4 ± 0.001E-4	2.671 ± 0.025	16.045 ± 1.9	15.29 ± 1.58	1.17E-3 ± 0.17E-3	7.18E-3 ± 2.73E-3	0.67 ± 0.05
1.41 V	0.05	-0.152E-4 ± 0.001E-4	3.26 ± 0.06	34.77 ± 20	65.18 ± 18.5	0.017 ± 0.01	2.7E-3 ± 2.34E-3	0.768 ± 0.125
	0.1	-0.158E-4 ± 0.005E-4	3.255 ± 0.001	35.16 ± 0.04	35.99 ± 0.99	0.494E-3 ± 0.005E-3	9.53E-3 ± 0.13E-3	0.594 ± 0.014
	0.2	-0.155E-4 ± 0.0001E-4	2.763 ± 0.003	3.57 ± 0.026	21.39 ± 0.02	0.179 ± 0.01	1.51E-3 ± 0.05E-3	0.873 ± 0.002

Table S6 Fitted results for electrochemical impedance spectroscopy measurement for Ni/C catalyst at I/C = 1 in 3.0 M KOH electrolyte with 0.1 M Urea.

	IPA/Water= 3/1 Loading(mg cm ⁻²)	I/C=1, 0.1 M Urea + 3M KOH						
		L (H)	R _s (Ω)	R _o (Ω)	R _{ct} (Ω)	C (F)	CPE (F s ⁻¹)	α
1.36 V	0.05	-0.298E-6 ± 0.13E-6	3.29 ± 0.01	55.63 ± 55.43	118.7 ± 47.23	0.294E-3 ± 0.06E-3	1.81E-3 ± 1.53E-3	0.805 ± 0.1
	0.1	-0.302E-6 ± 0.034E-6	2.694 ± 0.041	25.93 ± 16.38	43.12 ± 15.83	0.312E-3 ± 0.21E-3	6.85E-3 ± 6.1E-3	0.751 ± 0.15
	0.2	-0.216E-6 ± 0.03E-6	2.56 ± 0.04	17.12 ± 9.4	34.02 ± 8.5	0.065 ± 0.06	8.2E-3 ± 6.8E-3	0.738 ± 0.132
1.41 V	0.05	-0.326E-6 ± 0.023E-6	3.32 ± 0.03	243.2 ± 3.5	394.7 ± 11.9	2.709E-3 ± 2.44E-3	1.17E-3 ± 0.89E-3	0.835 ± 0.083
	0.1	-0.319E-6 ± 0.017E-6	2.73 ± 0.024	95.72 ± 3.8	167.95 ± 3.05	6.85E-3 ± 6.15E-3	2.69E-3 ± 2E-3	0.813 ± 0.09
	0.2	-0.25E-6 ± 0.01E-6	2.58 ± 0.016	51.16 ± 2.9	104.18 ± 8.62	8.8E-3 ± 7.25E-3	3.53E-3 ± 2.135E-3	0.818 ± 0.07

Table S7 Fitted results for electrochemical impedance spectroscopy measurement for Ni/C catalyst at I/C = 1 in 3.0 M KOH electrolyte with 1.0 M Urea.

	IPA/Water= 3/1 Loading(mg cm ⁻²)	I/C=1, 1 M Urea + 3M KOH						
		L (H)	R _s (Ω)	R _o (Ω)	R _{ct} (Ω)	C (F)	CPE (F s ⁻¹)	α
1.36 V	0.05	-0.329E-6 ± 0.05E-6	3.44 ± 0.06	56.22 ± 33	90.7 ± 31.7	0.019 ± 0.02	3.34E-3 ± 3.01E-3	0.759 ± 0.147
	0.1	-0.231E-6 ± 0.035E-6	2.79 ± 0.04	22.75 ± 13.6	36.74 ± 13.01	0.047 ± 0.04	7.8E-3 ± 7.2E-3	0.589 ± 0.005
	0.2	-0.0353E-6 ± 0.06E-6	4.204 ± 0.082	11.53 ± 7.42	20.03 ± 6.3	0.138 ± 0.1	0.02 ± 0.01	0.672 ± 0.2
1.41 V	0.05	-0.334E-6 ± 0.042E-6	3.446 ± 0.047	64.02 ± 21.95	106.69 ± 16.61	7.62E-3 ± 7.3E-3	2.75E-3 ± 2.45E-3	0.78 ± 0.13
	0.1	-0.233E-6 ± 0.03E-6	2.776 ± 0.034	26.11 ± 11.66	42.97 ± 9.8	0.023 ± 0.02	6.8E-3 ± 6.2E-3	0.76 ± 0.15
	0.2	-0.358E-6 ± 0.048E-6	4.211 ± 0.07	10.83 ± 5.8	20.12 ± 4.4	0.072 ± 0.07	0.016 ± 0.01	0.689 ± 0.183

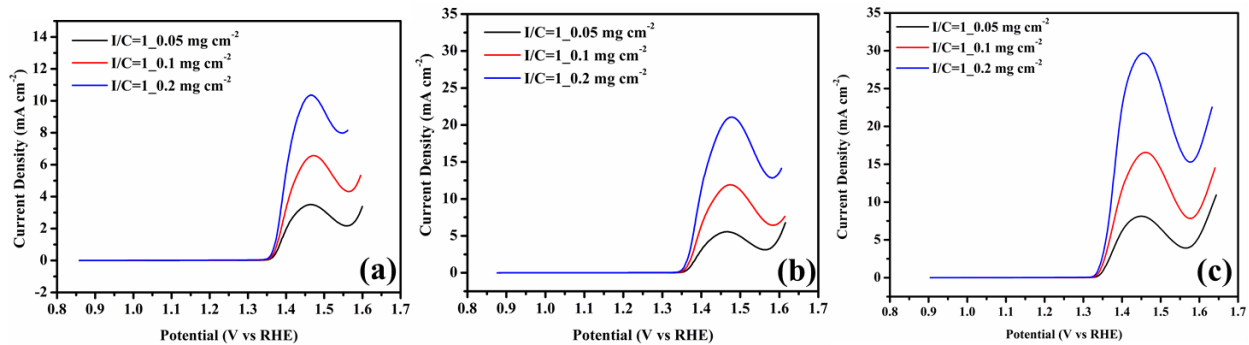


Figure S4. LSV curves of CLs at $I/C=1$ with different catalyst loading on the GCE obtained using 0.33 M urea in (a) 0.5 M (b) 1 M and (c) 3 M KOH at a scan rate of 10 mV s^{-1} .

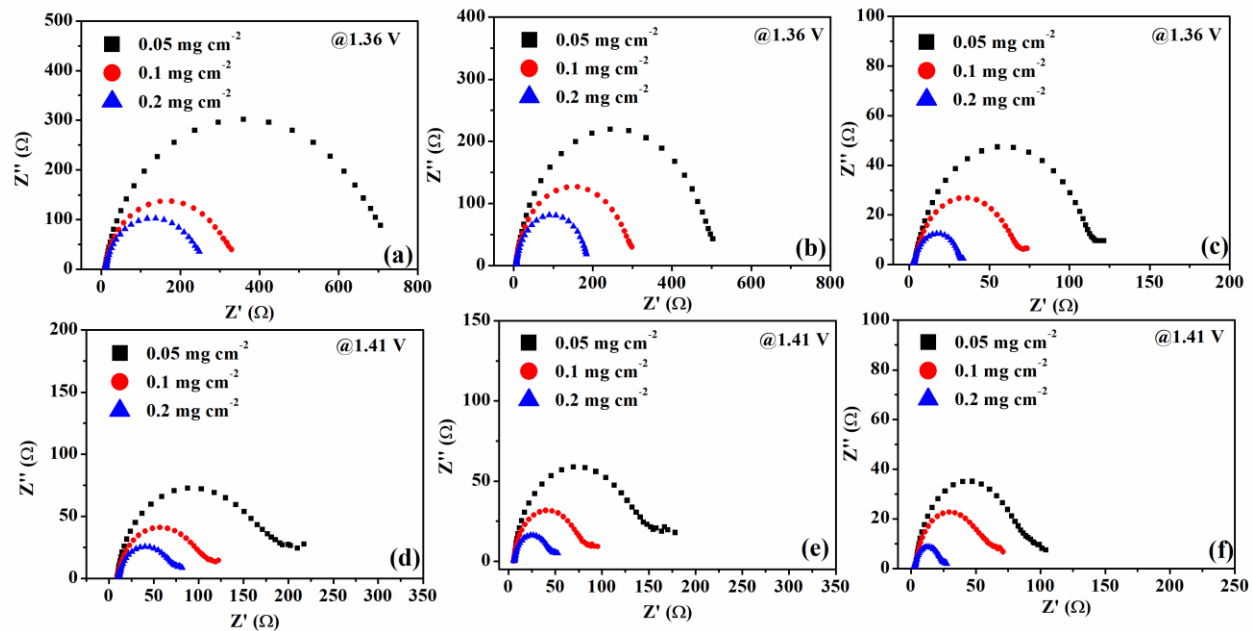


Figure S5. Electrochemical impedance spectra of the catalyst layers at $I/C=1$ ratio with different catalyst loading on the GCE obtained using 0.33 M urea in (a, d) 0.5 M (b, e) 1 M and (c, f) 3 M KOH.

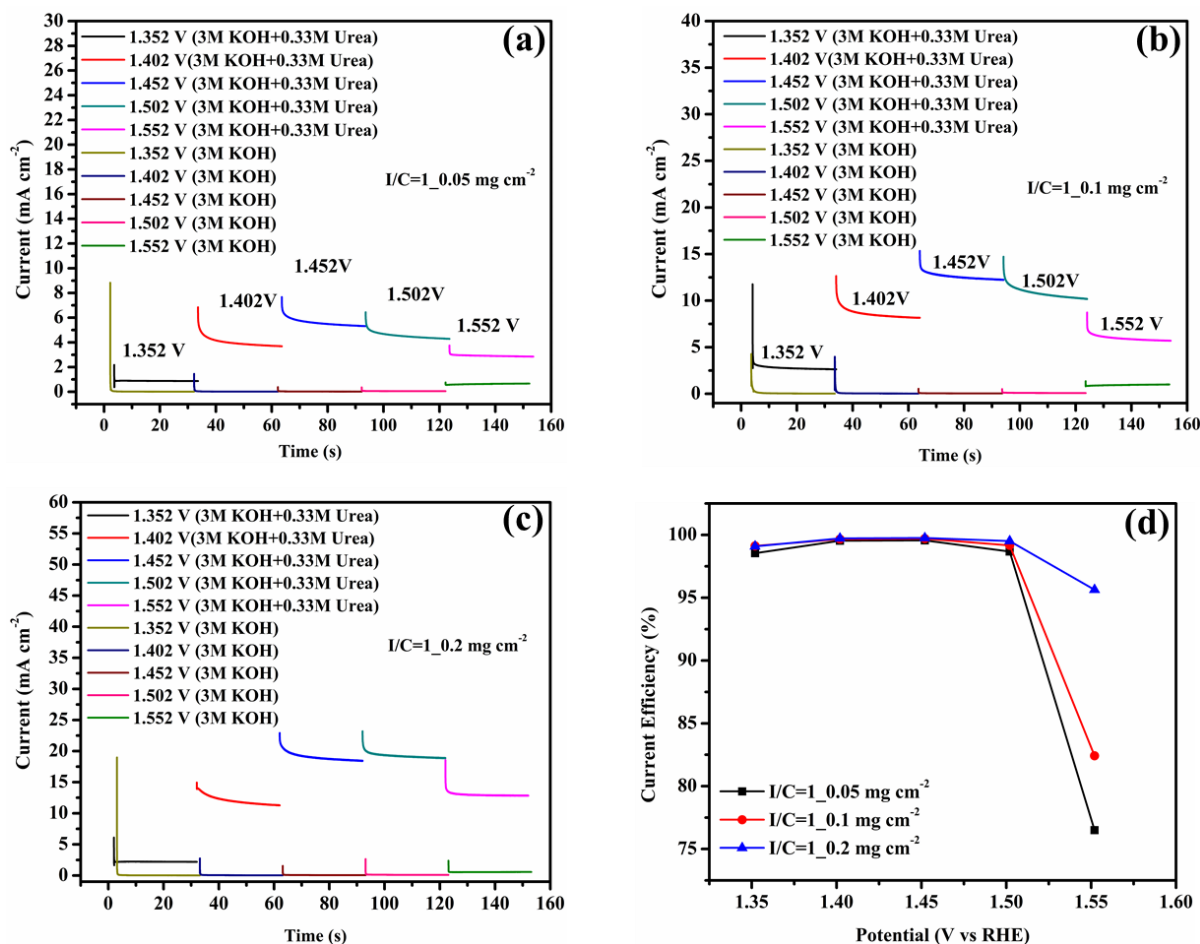


Figure S6. (a-c) Current density measured using step voltage method for the CLs at I/C=1 with different loading and (d) Measured Current Efficiency of the catalyst layers in 0.33 M urea in 3 M KOH.

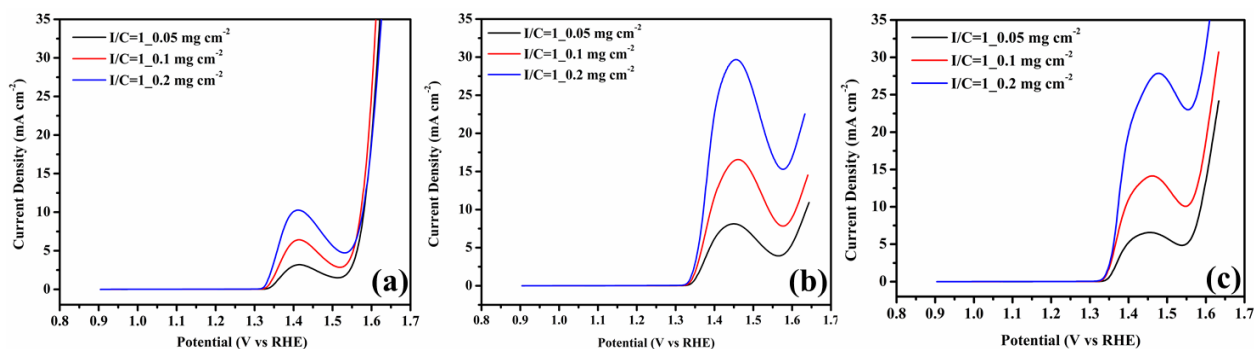


Figure S7. LSV curves of CLs at I/C = 1 with different catalyst loading on the GCE obtained in (a) 0.1 M (b) 0.33 M and (c) 1 M urea in 3 M KOH at a scan rate of 10 mV s⁻¹.

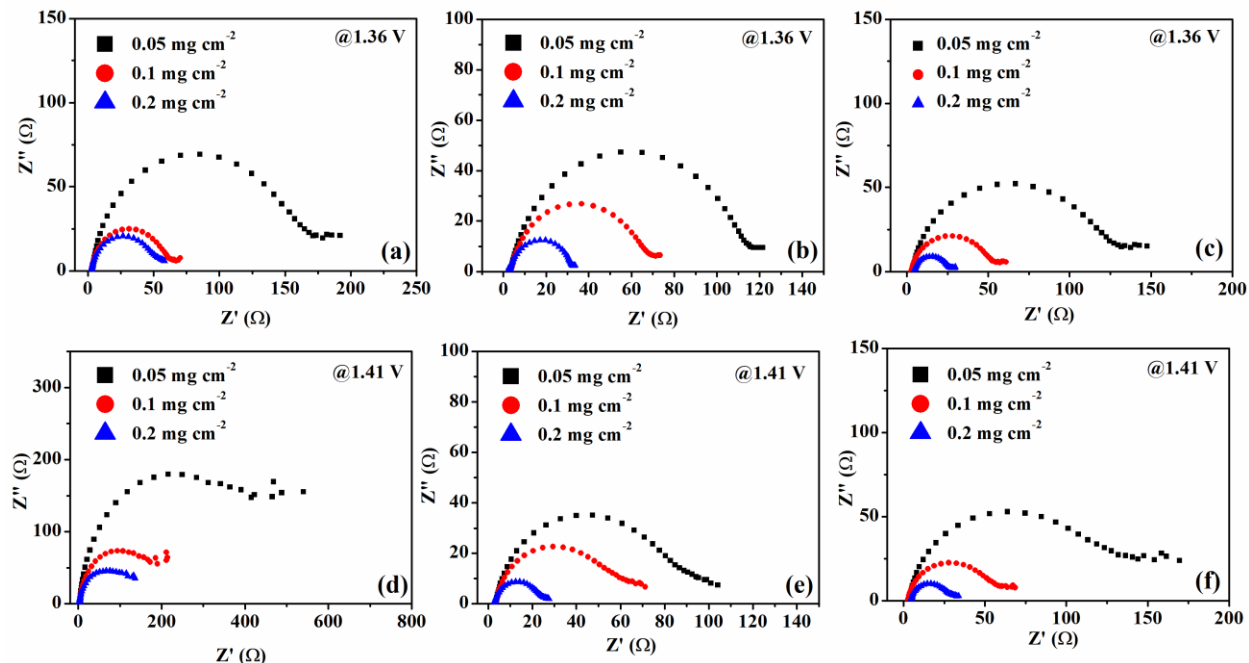


Figure S8. Electrochemical impedance spectra of the catalyst layers at I/C=1 ratio with different catalyst loading on the GCE obtained in (a, d) 0.1 M (b, e) 0.33 M and (c, f) 1 M urea in 3 M KOH.

Table S8: Potential (V vs RHE) at 10 mA mg⁻¹ and 200 mA mg⁻¹ for different catalyst layer compositions in urea in KOH solution.

Loading (mg cm ⁻²)	0.5 M KOH + 0.33 M Urea			1 M KOH + 0.33 M Urea	3 M KOH + 0.33 M Urea	3 M KOH + 0.1 M Urea	3 M KOH + 1 M Urea
	V vs RHE @ 10 mA mg ⁻¹			V vs RHE @ 10 mA mg ⁻¹	V vs RHE @ 10 mA mg ⁻¹	V vs RHE @ 10 mA mg ⁻¹	V vs RHE @ 10 mA mg ⁻¹
	I/C=1/8	I/C=1	I/C=3	I/C=1	I/C=1	I/C=1	I/C=1
0.05	1.362	1.358	1.356	1.350	1.332	1.332	1.334
0.1	1.357	1.359	1.353	1.351	1.330	1.327	1.330
0.2	1.358	1.360	1.358	1.351	1.331	1.324	1.333
Loading (mg cm ⁻²)	V vs RHE @ 200 mA mg ⁻¹			V vs RHE @ 200 mA mg ⁻¹	V vs RHE @ 200 mA mg ⁻¹	V vs RHE @ 200 mA mg ⁻¹	V vs RHE @ 200 mA mg ⁻¹
	I/C=1/8	I/C=1	I/C=3	I/C=1	I/C=1	I/C=1	I/C=1
	I/C=1/8	I/C=1	I/C=3	I/C=1	I/C=1	I/C=1	I/C=1
0.05	1.406	1.399	1.399	1.384	1.362	1.372	1.364
0.1	1.387	1.406	1.404	1.384	1.361	1.366	1.361
0.2	-	1.415	1.412	1.386	1.366	1.373	1.368

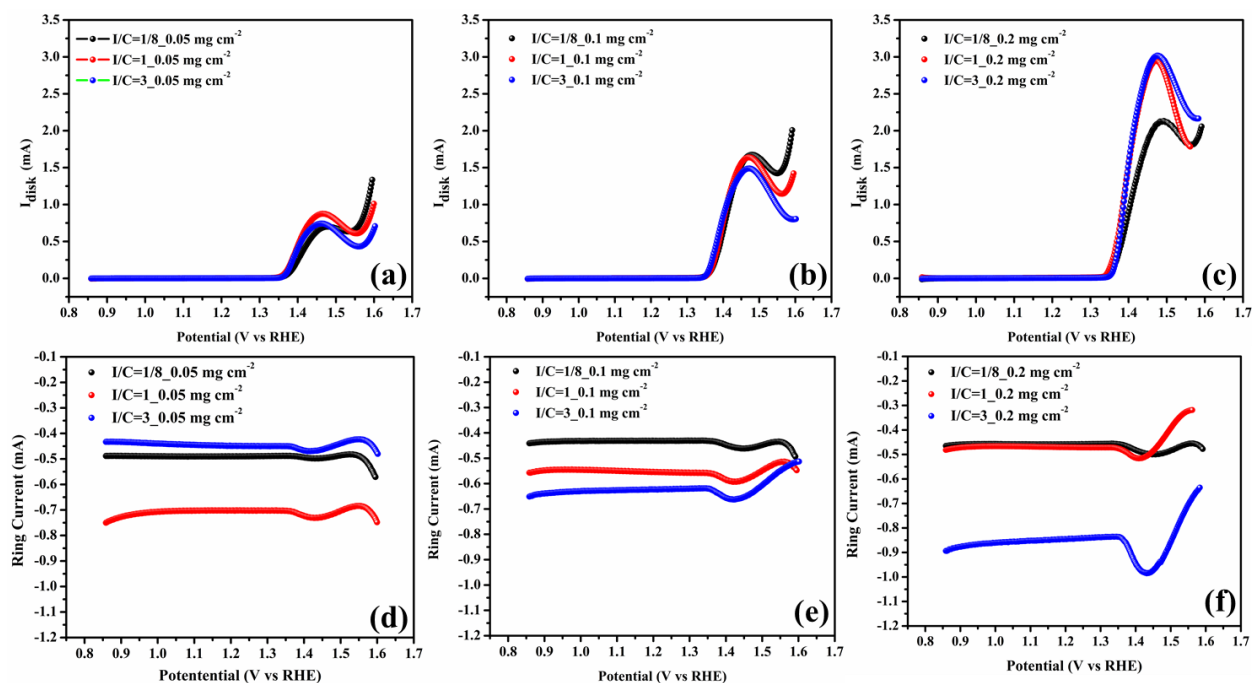


Figure S9. RRDE results showing the (a-c) disk current and the corresponding (d-f) ring current with different I/C ratios and catalyst loadings in 0.33 M urea and 0.5 M KOH.

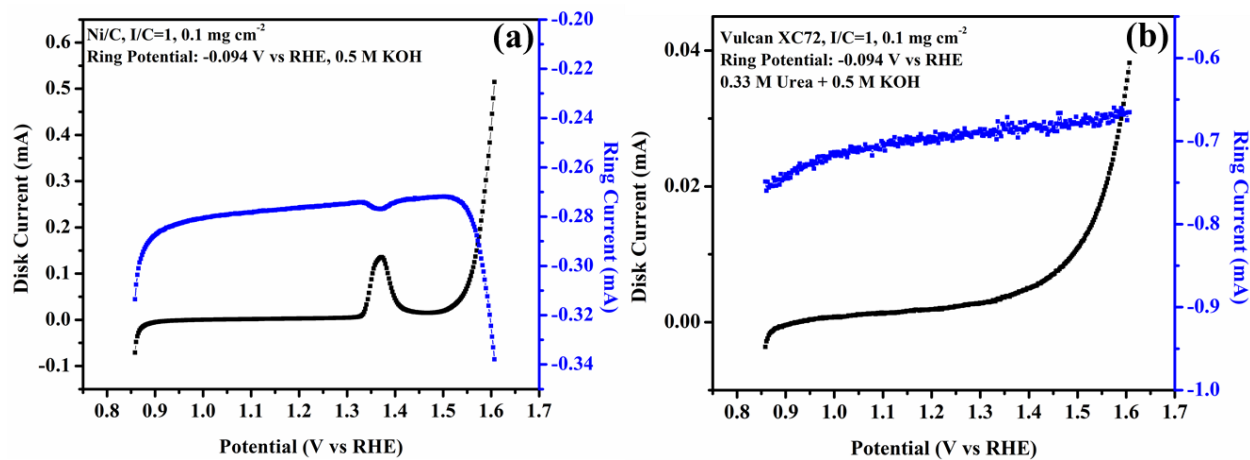


Fig. S10. RRDE results of the disk current and the corresponding ring current of (a) Ni on Vulcan XC 72 in 0.5 M KOH solution and (b) Vulcan XC 72 in 0.33 M urea in 0.5 M KOH at a scan rate of 20 mV s^{-1} and ring potential of -0.094 V .

RRDE study: Derivation of OH⁻ activity change using Butler-Volmer kinetic equation.

$$i_1 = i_0 \times rf \times \left[e^{\alpha n F \eta / RT} - \left(\frac{a_{1,H_2}}{a_{H_2}^*} \right)^{0.5} \left(\frac{a_{1,OH^-}}{a_{OH^-}^*} \right) e^{-(1-\alpha)n F \eta / RT} \right] \quad (S1)$$

$$i_2 = i_0 \times rf \times \left[e^{\alpha n F \eta / RT} - \left(\frac{a_{2,H_2}}{a_{H_2}^*} \right)^{0.5} \left(\frac{a_{2,OH^-}}{a_{OH^-}^*} \right) e^{-(1-\alpha)n F \eta / RT} \right] \quad (S2)$$

$$\frac{i_2}{i_1} = \frac{\left[1 - \left(\frac{a_{2,OH^-}}{a_{OH^-}^*} \right) e^{-n F \eta / RT} \right]}{\left[1 - \left(\frac{a_{1,OH^-}}{a_{OH^-}^*} \right) e^{-n F \eta / RT} \right]} \text{ where } \left(\frac{a_{1,H_2}}{a_{H_2}^*} \right) = \left(\frac{a_{2,H_2}}{a_{H_2}^*} \right) = 1 \quad (S3)$$

$$e^{-n F \eta / RT} = 0.026 \quad (n = 1, \eta = 0.094 \text{ V}, T = 25^\circ\text{C}) \quad (S4)$$

$$\frac{i_2}{i_1} = \frac{\left[1 - 0.026 a_{2,OH^-} \right]}{\left[1 - 0.026 a_{1,OH^-} \right]} \text{ where } a_{OH^-}^* = 1 \quad (S5)$$

$$\frac{i_2}{i_1} - \frac{i_2}{i_1} (0.026 a_{1,OH^-}) = 1 - 0.026 a_{2,OH^-} \quad (S6)$$

$$a_{2,OH^-} = \frac{\left[\frac{i_2}{i_1} (0.026 a_{1,OH^-}) - \frac{i_2}{i_1} + 1 \right]}{0.026} \quad (S7)$$