Supplementary Information

for

Direct Nitrile Electrosynthesis from Amino Acids on Nickel Oxyhydroxide

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Experimental Section

Chemicals

All reagents were used as received without further purification. Ammonia solution (NH3·H2O, 28%), potassium hydroxide (KOH, 95%), nickel acetate tetrahydrate ($Ni(OAc)_2$·4H2O, 99.9%), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, 98%), alanine (Ala, 99%), glutamic acid (Glu, 99.9%), lysine (Lys, 99%), leucine (Leu, 99%), valine (Val, 98%), aspartic acid (Asp, 98%), arginine (Arg, 98%), phenylalanine (Phe, 98%), 3-amino-3-methylbutanoic acid (97%), 2-NH_2-isobutyric acid (98%), 2-OH-isobutyric acid (98%), isopropylamine (99%), propionic acid (99.5%), tert-butylamine (99.5%), N,N-dimethylglycine (98%), N-methyl-alanine (98%), acetonitrile (99.5%), acetic acid (99.8%), acetamide (99%), glutaronitrile (96%), glutaric acid (99%), isovaleronitrile (98%), isobutyronitrile (99.2%), cyanoacetic acid (98%), 3-cyanopropanoic acid (98%), isobutyl methyl ketone (98%), chloroform (99%), ethylacetate (99.5%), tetrahydrofuran (THF, 99%), N,N-dimethylformamide (DMF, 99.5%) and fumaric acid (99.5%) were purchased from Aladdin Industrial Corporation (China). Sulfuric acid (H2SO4, CP) was purchased from Shanghai Test Agent Co., Ltd. (China). Platinum sheet and Ag/AgCl electrodes were purchased from Wuhan GaossUnion Technology Co., Ltd. (China). Carbon fiber paper was purchased from Hesen Electric Co. Ltd. (HCP020N, China). Ultrapure deionized water (18.2 MΩ·cm–1, 25 °C) was obtained from ELGA purification system (China).

Catalyst Electrode Preparation

For β-$Ni(OH)_2$, 0.3981 g $Ni(OAc)_2$·4H2O (1.6 mmol) was completely dissolved in 8 mL H_2O. Then 80 mL DMF was added to the solution and reacted at 90 °C for 4 hours. The mixture was then centrifugated, washed with deionized water for three times and dried at 60 °C overnight. The obtained green powder is the β-$Ni(OH)_2$.

For NiO-Ar, β-$Ni(OH)_2$ was annealed at 300 °C for 1 hour under Ar atmosphere with the ramping rate of 5 °C min^{-1}. the obtained black powder is the NiO-Ar.

For α-$Ni(OH)_2$, an electrodeposition method with a three-electrode configuration was employed. 0.1 M $Ni(NO_3)_2$ aqueous solution was used as the electrolyte. Carbon fiber paper (CFP, 1×2 cm^2) was used as the working electrode, which was ultrasonically washed with acetone, 0.1 M HCl and deionized water before use. Graphite rod was used as the counter electrode. The electrodeposition was carried out under a constant cathodic current density of 10 mA cm^{-2} for 120 s. After the electrodeposition, the electrode was rinsed with deionized water, and then dried at 60 °C before the electrochemical measurement.

Electrochemical Measurements

The electrochemical measurements were performed on a CHI 660E workstation using a typical H-type electrochemical cell with a three-electrode system. The as-prepared catalysts on carbon fiber paper were served as the working electrode. A Pt sheet (1 cm × 2 cm) and Ag/AgCl electrode in saturated KCl solution were used as the counter electrode and the reference electrode, respectively. Applied potentials were converted to RHE scale according to following equation unless otherwise specified:

$$E(RHE) = E(Ag/AgCl) + 0.197 + 0.0591 \times pH\#(1)$$

The electrochemical oxidation activity was evaluated in a solution of 0.1 M substrate and 1 M KOH. The linear sweep voltammetry (LSV) curves were scanned at a rate of 1 mV s^{-1} at room temperature after 5 cyclic voltammetry (CV) cycles at a scan rate of 50 mV s^{-1}.

In the electro-oxidation experiment, a constant potential of 1.42 V *vs.* RHE was applied for 3 hours at room temperature in a solution of 0.1 M substrate and 1 M KOH, unless otherwise specified. The kinetic study was conducted under similar conditions, with sample analyzed at specific intervals to stimulate the reaction order and rate constant.

Electrolysis Product Analysis

The obtained products were identified by ^1H NMR spectroscopy on a Bruker AVANCE III HD (400 MHz) spectrometer. To detect the potential trace ammonia, we sampled part of the electrolyte for acidification (500 μL electrolyte + 111 μL 5 M H_2SO_4) immediately after the reaction for analysis. For the determination of corresponding nitriles, 100 μL of the obtained acidified electrolyte was added with 500 μL of D2O containing 1.16 mg fumaric acid (10 μmol) as an internal standard. The mole numbers of the product were calculated through the standard curves.

The product FE was calculated through the following equation:

$$\mathrm{FE}(\%) = \frac{\mathrm{n_{nitrile}} \times \mathrm{z_{nitrile}} \times \mathrm{F}}{\mathrm{Q_{total}}} \times 100\%\#(2)$$

where $z_{nitrile}$ = 4 (for most amino acids) or 8 (for Lys) is the number of electrons required to produce corresponding nitriles, F is the faradaic constant (96,485 C mol^{-1}), and Q_{total} is the total charge.

The yield rate was calculated through the following equation:

$$\text{Yield rate}(mmolmg_{cat}^{-1}h^{-1}) = \frac{\mathrm{n_{nitrile}}}{\mathrm{t} \times \mathrm{m_{catalyst}}}\#(3)$$

where t is the time of electrolysis, $m_{catalyst}$ is the mass of electrocatalyst.

The conversion of Ala was calculated through the following equation:

$$\mathrm{Conversion}(\%) = \frac{\mathrm{c_{Ala}}}{\mathrm{c_{substrate}}} \times 100\%\#(4)$$

where c_{Ala} is the concentration of Ala after electrolysis and $c_{substrate}$ is that of Ala before electroltysis.

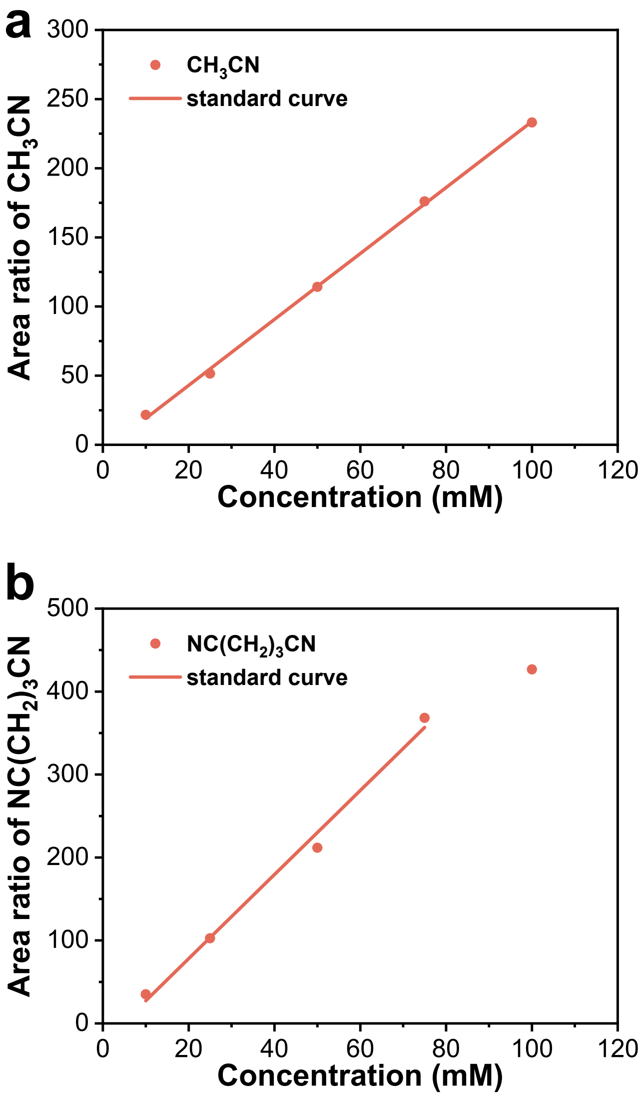
The selectivity of glutaronitrile was calculated through the following equation:

$$\mathrm{Selectivity}(\%) = \frac{\mathrm{c_{glutaronitrile}}}{\mathrm{c_{glutaronitrile}} + \mathrm{c_{glutaric\ acid}}} \times 100\%\#(5)$$

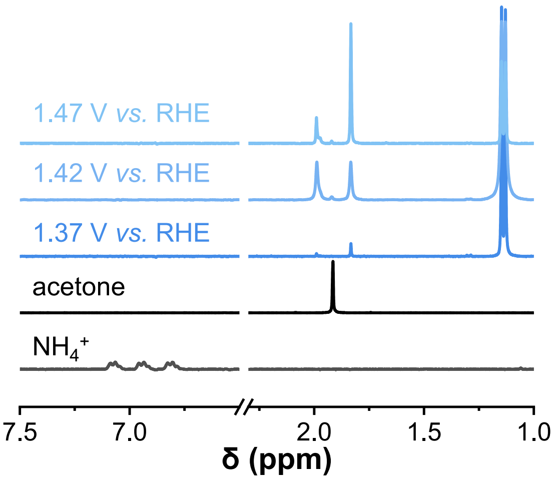
where $c_{glutaronitrile}$ is the concentration of glutaronitrile and $c_{glutaric\ acid}$ is the concentration of glutaric acid.

In Situ ATR-SEIRAS Measurement

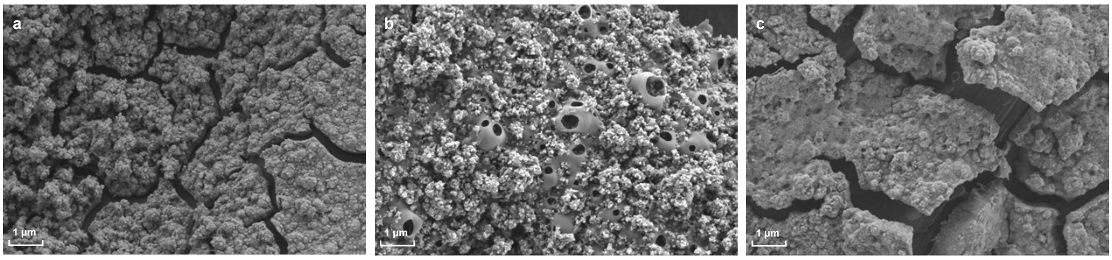
The Au-coated Si prism was used as the working electrode, with the Ag/AgCl electrode and the Pt foil as the reference and counter electrodes, respectively. Time-dependent and potential-dynamic measurement was conducted in the N2-saturated atmosphere, and ∼10 sccm N2 flow was kept bubbling through the spectro-electrochemical cell and infrared spectrometer. ATR spectra were acquired at a resolution of 4 cm^{-1} with unpolarized IR radiation at an incidence angle of ca. 60° by a Nicolet iS20 FTIR spectrometer (Nicolet iS20 FTIR, Thermo Scientific) with a builtin MCT detector. All spectra were converted to the absorbance unit as −log (I/I_0), where I and I_0 represent the signal intensities of the reflected radiation of the sample and reference spectra. The electrochemical workstation (CHI 660E, Shanghai CH Instruments Co., China) was utilized for the potential control.



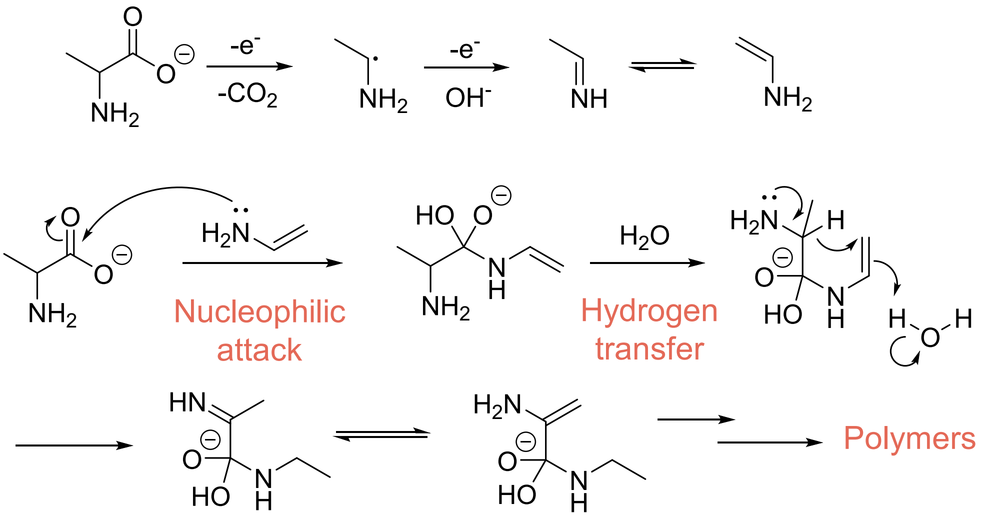
Supplementary Figure 1. (a) Standard curve of acetonitrile. Area ratio = 2.38 concentration (mM) – 4.70. (b) Standard curve of glutaronitrile. Area ratio = 5.07 concentration (mM) – 23.30.



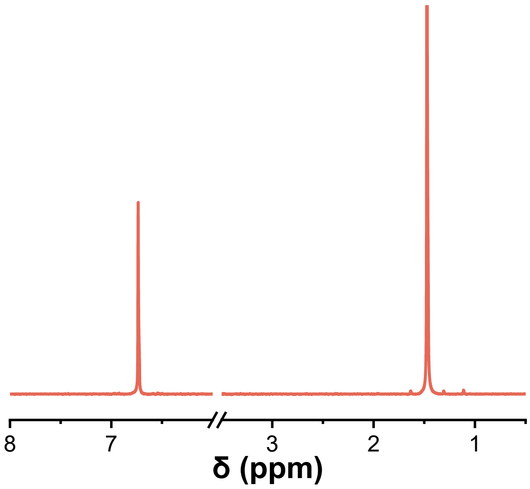
Supplementary Figure 2. ^{1}H NMR spectra of electrolysis products of Ala on β-Ni(OH)$_2$ at different potentials.



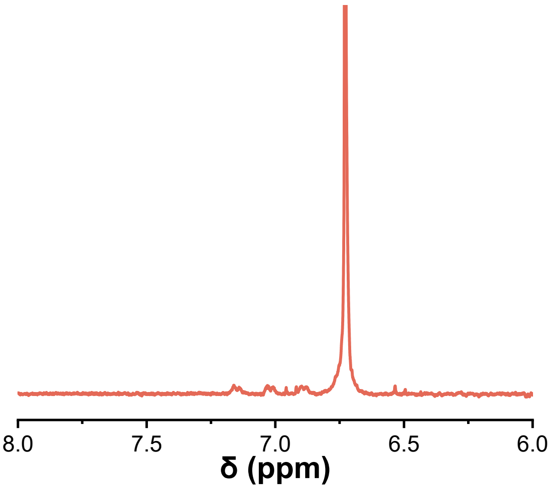
Supplementary Figure 3. SEM images of the electrode (a) before electrolysis and after electrolysis of (b) Phe or (c) methionine (Met).



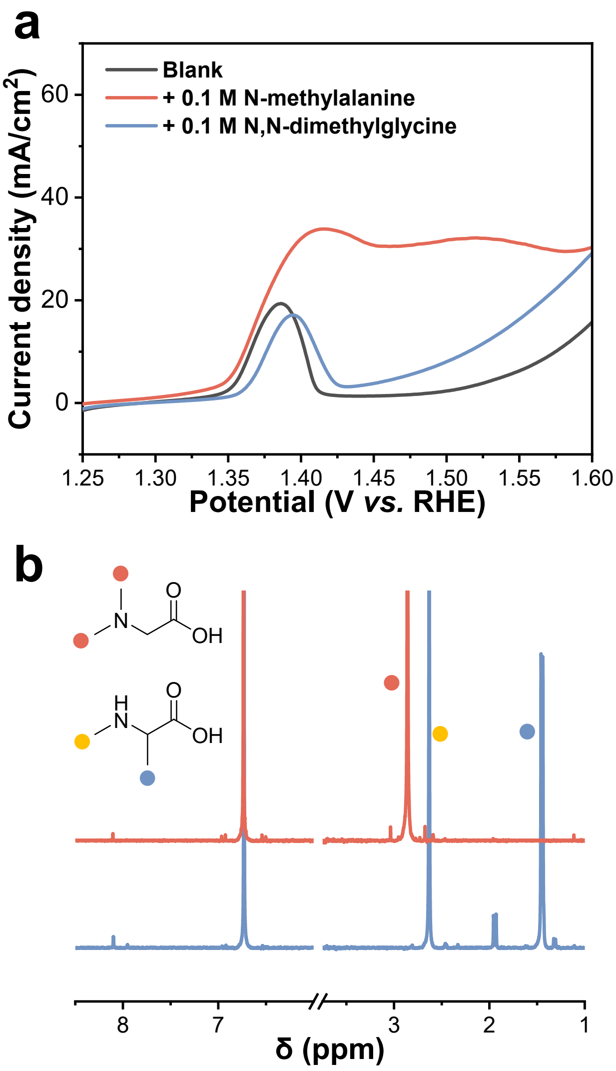
Supplementary Figure 4. Probable mechanism of anodic bias-driven polymerization



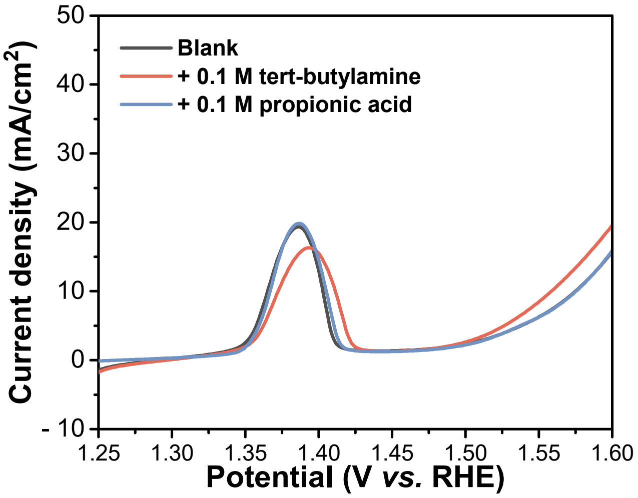
Supplementary Figure 5. ^{1}H NMR spectra of 0.1 M 2-NH_2-isobutyric acid. The peak at 6.72 ppm belongs to the internal standard fumaric acid.



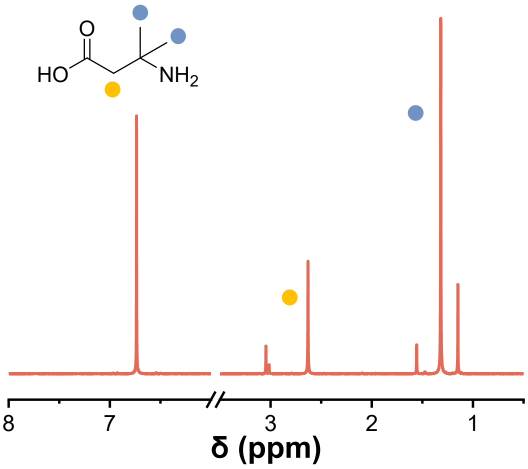
Supplementary Figure 6. ^{1}H NMR spectra of the solution containing 1 mM NH_4^+. The peak at 6.72 ppm belongs to the internal standard fumaric acid, and the triplet peaks around 7 ppm belong to NH_4^+.



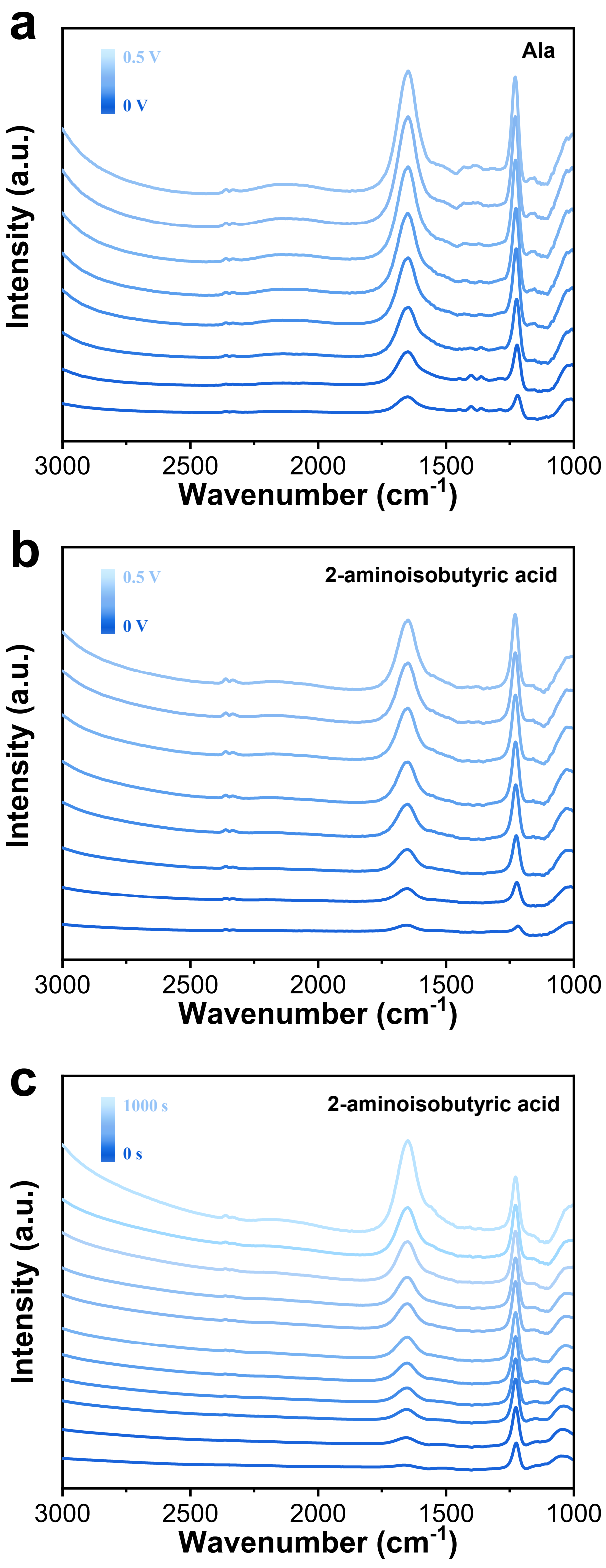
Supplementary Figure 7. (a) Polarization curves of N-methylalanine and N,N-dimethylglycine in 1 M KOH. (b) ^{1}H NMR spectra of electrolysis products of N-methylalanine (blue) and N,N-dimethylglycine (red) at 1.42 V *vs.* RHE. The peak at 6.72 ppm belongs to the internal standard fumaric acid.



Supplementary Figure 8. Polarization curves of 0.1 M tert-butylamine and propionic acid in 1 M KOH.

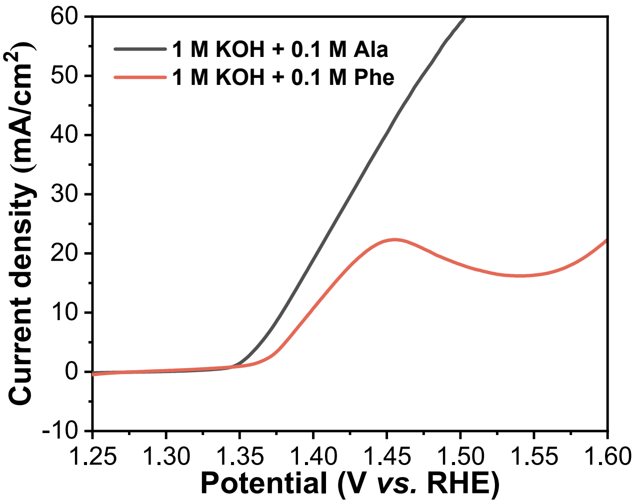


Supplementary Figure 9. ^{1}H NMR spectra of electrolysis products of AMBA at 1.42 V *vs.* RHE. The peak at 6.72 ppm belongs to the internal standard fumaric acid.

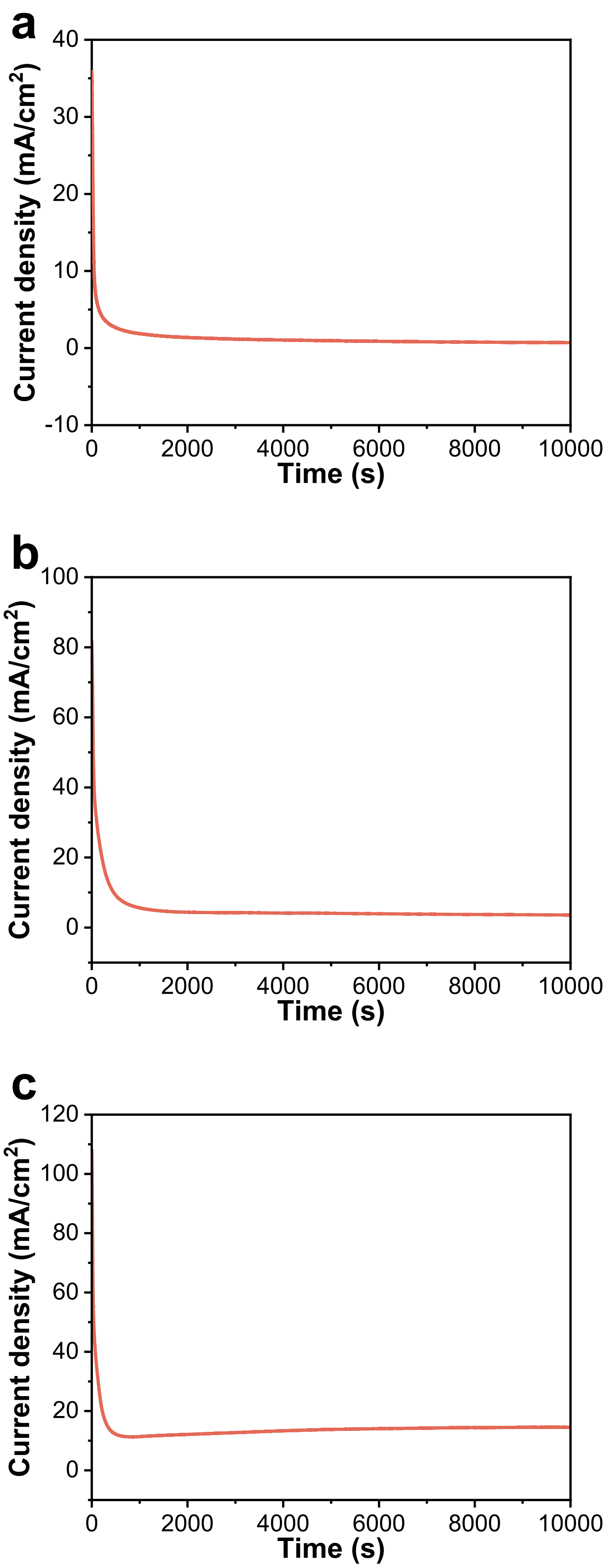


Supplementary Figure 10. (a) Potential-dependent ATR-SEIRAS spectra of 0.1 M Ala in 1 M KOH. (b) Potential-dependent ATR-SEIRAS spectroscopy of 0.1 M 2-NH_2-isobutyric acid in 1 M KOH. (c) Time-dependent ATR-SEIRAS spectroscopy of 0.1 M 2-NH_2-isobutyric acid in 1 M

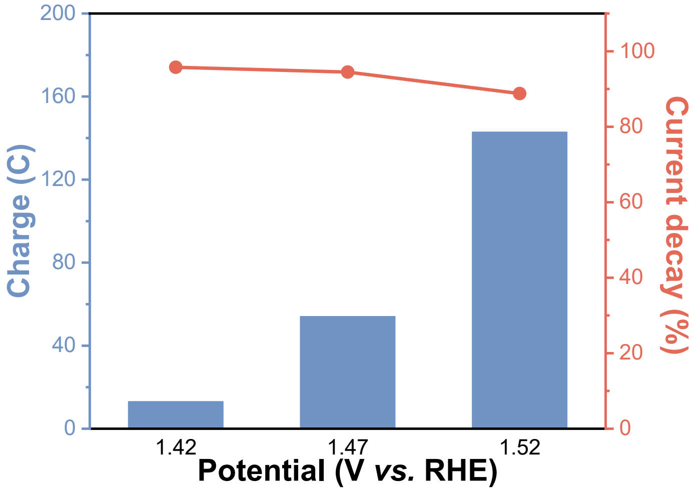
KOH.



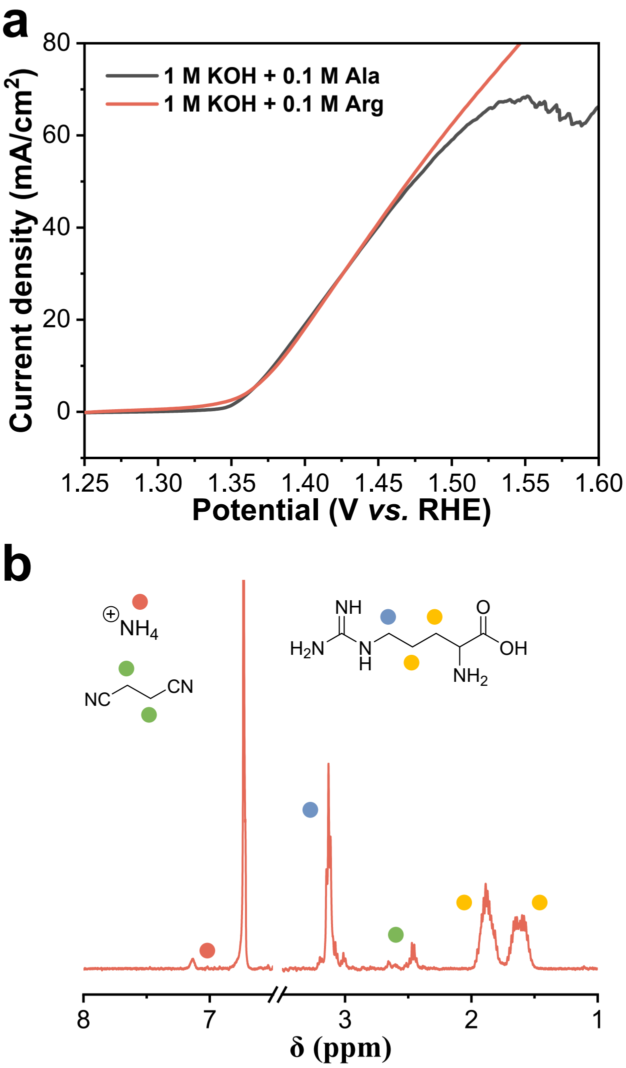
Supplementary Figure 11. Polarization curve of 0.1 M Phe in 1 M KOH compared to that of 0.1 M Ala in 1 M KOH.



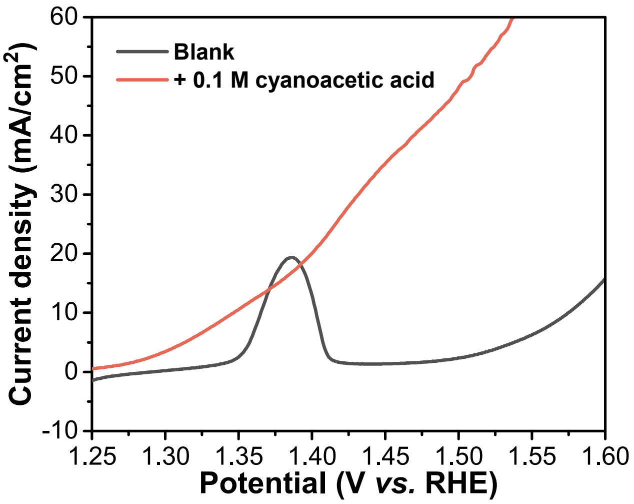
Supplementary Figure 12. i-t curves of 0.1 M Phe in 1 M KOH during constant-potential electrolysis at (a) 1.42 V *vs*. RHE (b) 1.47 V *vs*. RHE (c) 1.52 V *vs*. RHE.



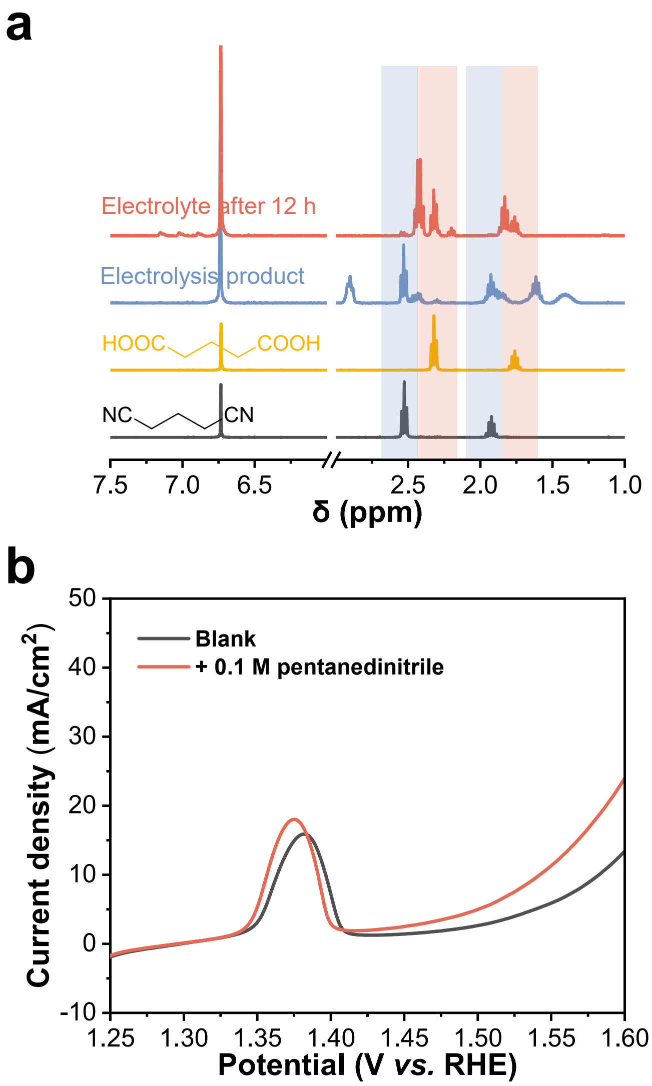
Supplementary Figure 13. Total charge in 3 h and current decay in 0.5 h of Phe electrolysis under different potentials.



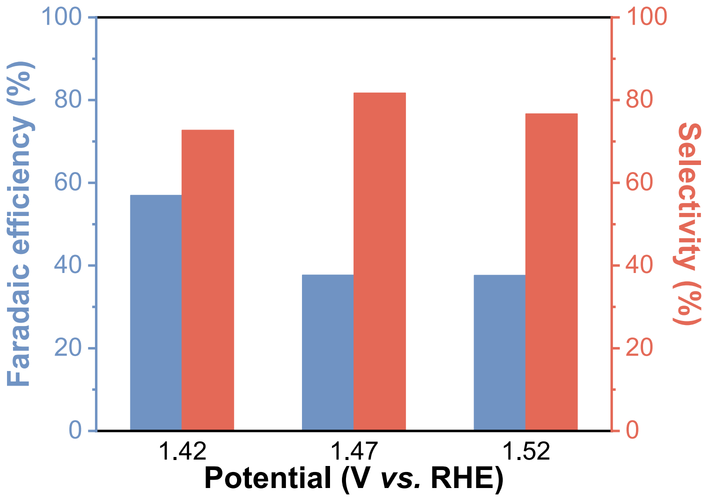
Supplementary Figure 14. (a) Polarization curves of 0.1 M Arg in 1 M KOH. (b) ^{1}H NMR spectra of electrolysis products of Arg at 1.42 V *vs.* RHE. The peak at 6.72 ppm belongs to the internal standard fumaric acid.



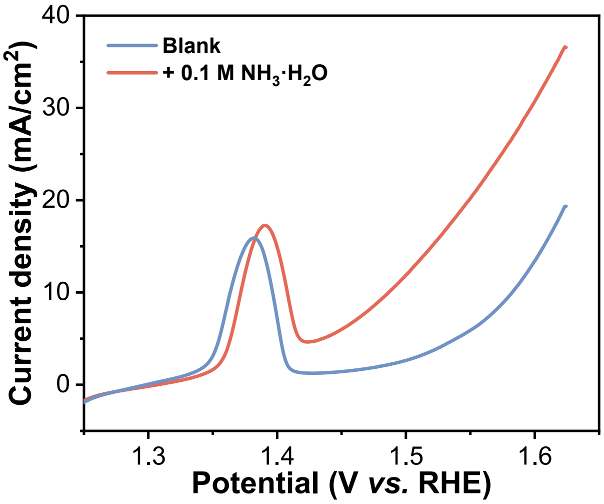
Supplementary Figure 15. Polarization curve of 0.1 M cyanoacetic acid in 1 M KOH.



Supplementary Figure 16. (a) ^{1}H NMR spectra of glutaronitrile (black), glutaric acid (yellow), electrolyte of 0.1 M Lys and 1 M KOH after electrolysis (blue) and a solution of 0.1 M Lys and 1 M KOH standing after 12 hours (red). The peak at 6.72 ppm belongs to the internal standard fumaric acid. (b) Polarization curve of 0.1 M glutaronitrile and 1 M KOH.

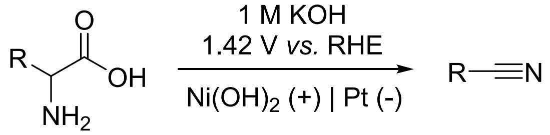


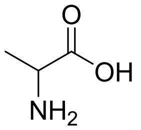
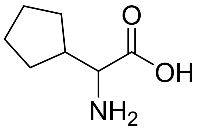
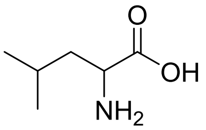
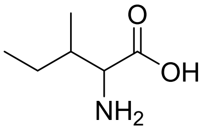
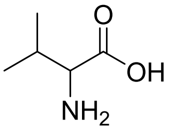
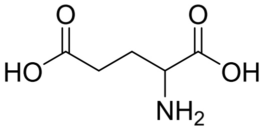
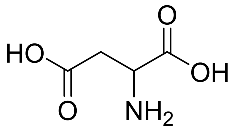
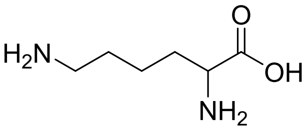
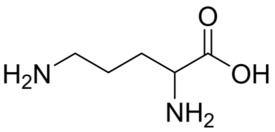
Supplementary Figure 17. FEs and selectivities of 0.1 M Lys under different anodic potential.

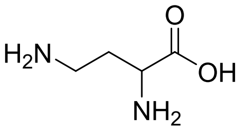
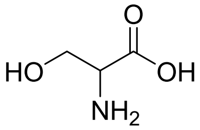
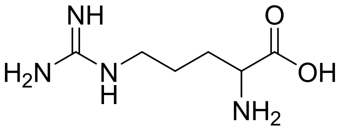
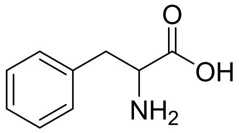
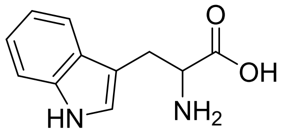
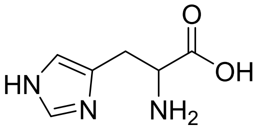
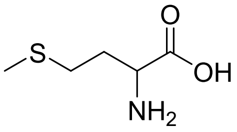
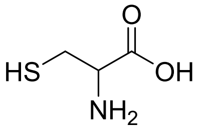


Supplementary Figure 18. Polarization curve of 0.1 M $NH_3 \cdot H_2O$ and 1 M KOH.

Table 1 FEs of the oxidation of different amino acids



Substrate	FE (%)
	87.1
	94.9
	83.8
	50.1
	53.5
	91.9
	19.6
	63.0
	42.0

	0.00
	35.0 (Formate)
	3.20
	0.00
	0.00
	0.00
	0.00
	0.00