Supporting Information

Kraft Lignin Electro-Oxidation under Ambient Temperature and Pressure

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Cell setup

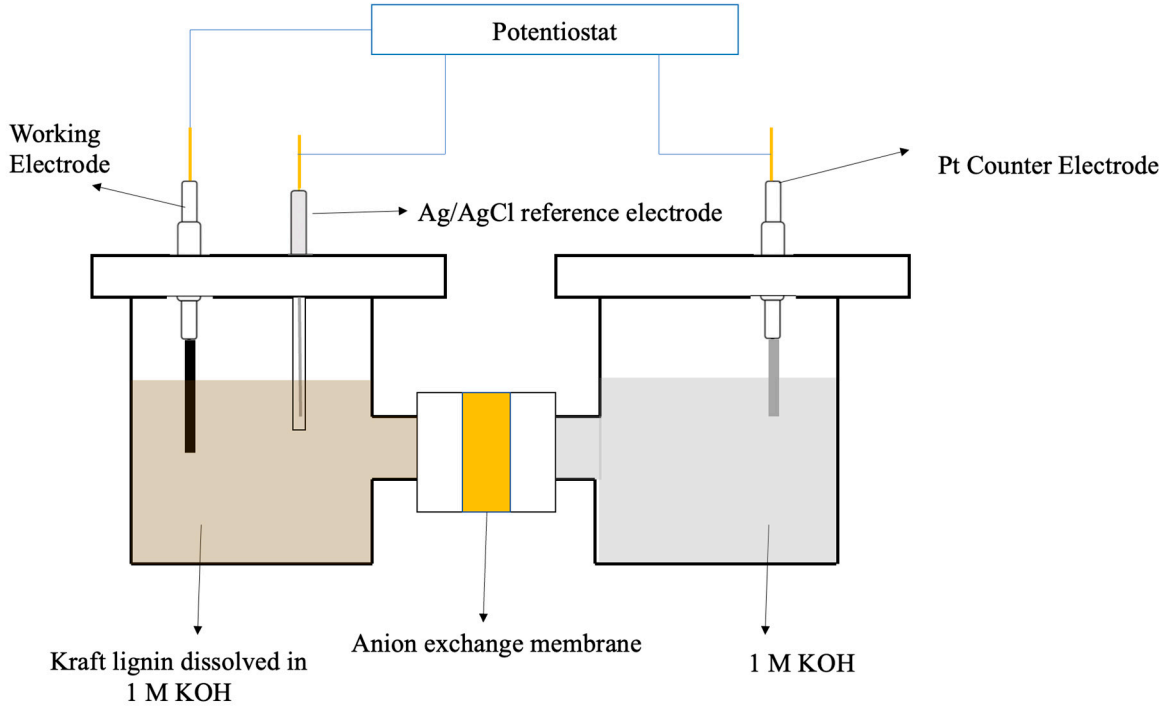

Figure S1. H-cell configuration for Kraft lignin oxidation with 1 M KOH on both sides of the cell

Product analysis

1 Liquid-Liquid Extraction and Rotary Evaporation

After the reaction, 25 mL of the lignin solution was taken from the H-cell and acidified with a 1:1 volume ratio of 1 M H_2SO_4 so that the unreacted lignin solid could be precipitated out.

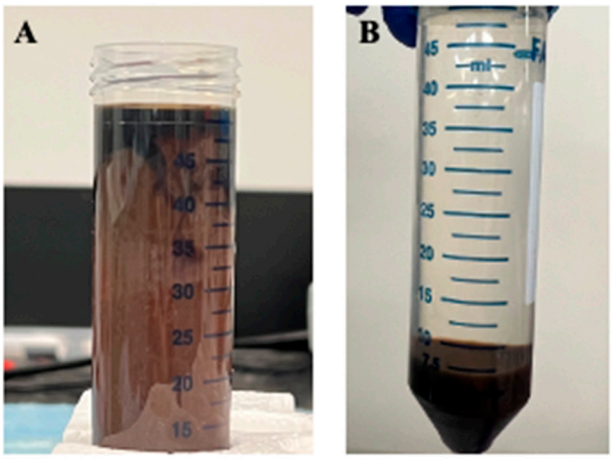

Figure S2. Lignin solution acidified with an equal volume of 1 M H_2SO_4, before (A) and after (B) centrifuge.

To accelerate the solid-liquid separation, the mixture was then centrifuged with a Beckman Coulter Allegra® X-12R centrifuge at 3500 rpm and 25 ℃ for 15 minutes. According to the literature, the most commonly used extraction solvents are ethyl acetate,[9] dichloromethane,[48] chloroform.[12,17] In this project, dichloromethane was selected as the organic solvent for product extraction. After the centrifuge, 20 mL of the clear solution was transferred into a separation funnel and extracted with 20 mL HPLC-grade dichloromethane for three times (60 mL in total). The organic phase from liquid-liquid solvent extraction was collected from the bottom of the separation funnel and put through a fine filter paper filled with sodium sulfate anhydrous to remove the moisture as well as to remove the small lignin solid particle remainder from the centrifuge.

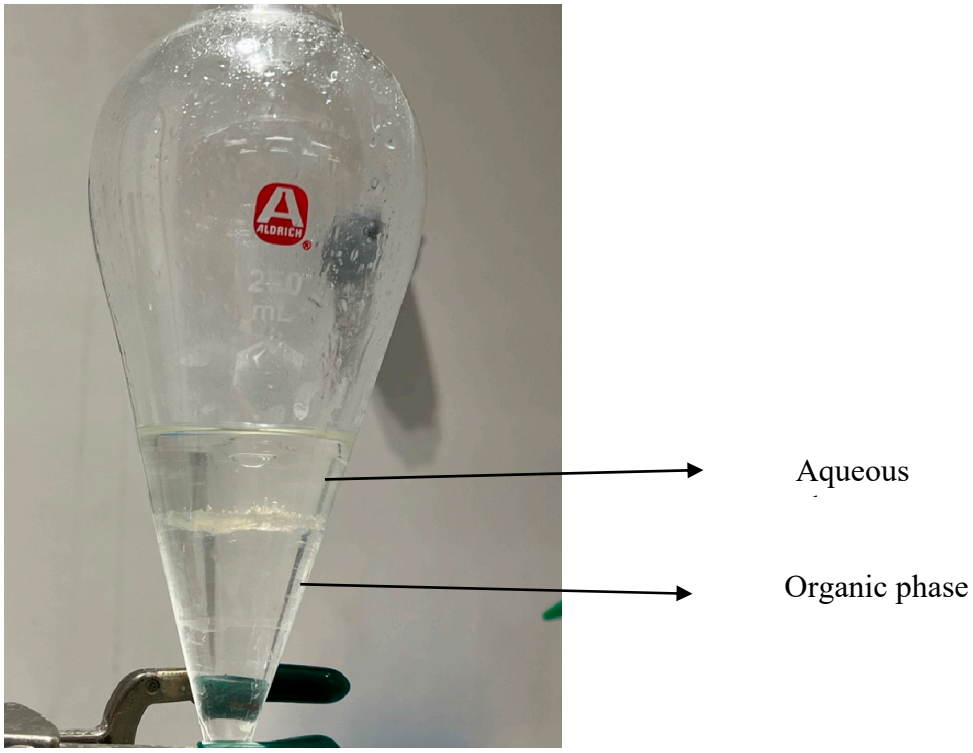

Figure S3. Separation funnel with aqueous phase (product solution from centrifuge) on top and organic phase (dichloromethane) at the bottom

The filtered organic solution was then put into a BUCHI® R-210 rotary evaporation system with a water bath at 47 ℃, pressured at 773 mbar, and the coolant temperature set at 18 ℃. After around 10 minutes, a dried light-brown solid was seen at the bottom of the evaporation flask. The dried solution was then re-concentrated in 3 mL of HPLC-grade dichloromethane before entering GC-MS.

2 GC-MS

Gas chromatography (GC) is widely utilized in the field of lignin valorization. It is a common type of chromatography used for separating and analyzing the products retained from the degraded lignin.

The GC method was used in this project is GC-MS (Gas Chromatography-Mass Spectrometry). GC-MS is widely used in the lignin valorization field to identify the product species. The GC-MS was performed on Agilent 6890N with a Rxi-5ms column (length: 30 m, inner diameter: 0.25 mm, film, 0.25 μm) with an Agilent 5975B MS detector. The GC-MS test runs for 26 minutes with an initial temperature of 40 ℃ and the temperature increases at a rate of 15 ℃/min and the temperature is maintained at 250 ℃ until the end of the analysis. Helium was used as the carrier gas at a flow rate of 1.5 mL/min. The ion masses were recorded in the range of 40 to 300 (m/z) in the scan mode. The detected compounds were identified according to the NIST library database. As the reaction time of 1500 s was not long enough for the system to generate enough products to significantly differentiate the products with small yields from the noises, to enlarge the absolute product yield. The electro-oxidative reaction was performed in the same H-cell described above under 1 V vs Ag/AgCl electrode for 10 hours and Ni foam was used for the GC-MS product preparation.

GC-MS chromatogram

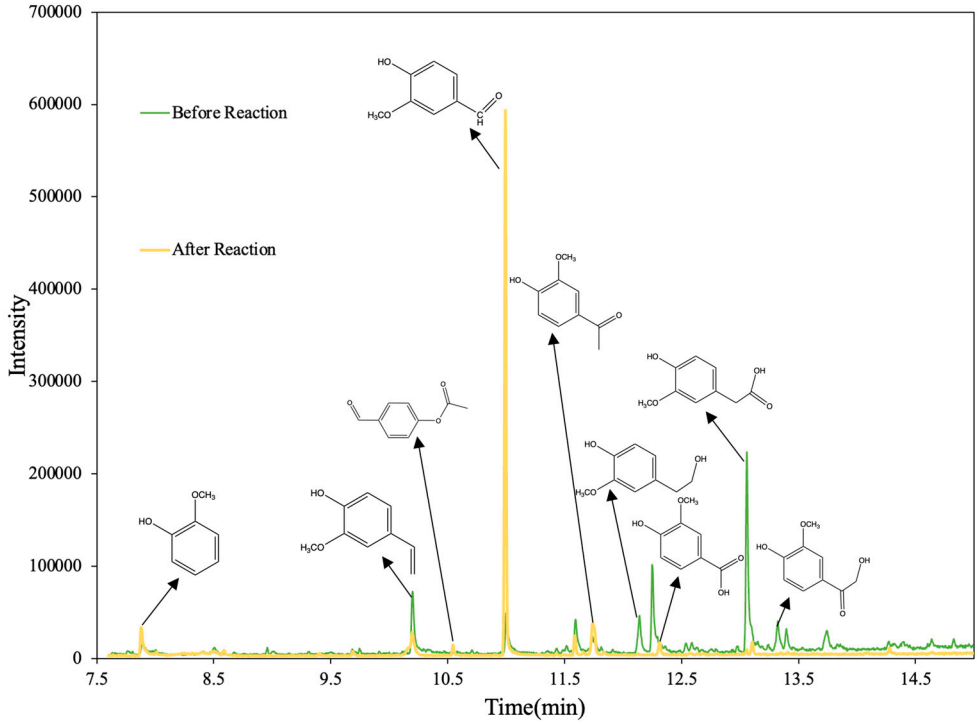

Figure S4. GC-MS Chromatogram of extracted lignin products before (green) and after (yellow) reaction. This is the GC-MS chromatogram showing the identified chemical species with their respective retention times.

Vanillin and Vanillic acid HPLC calibration curve

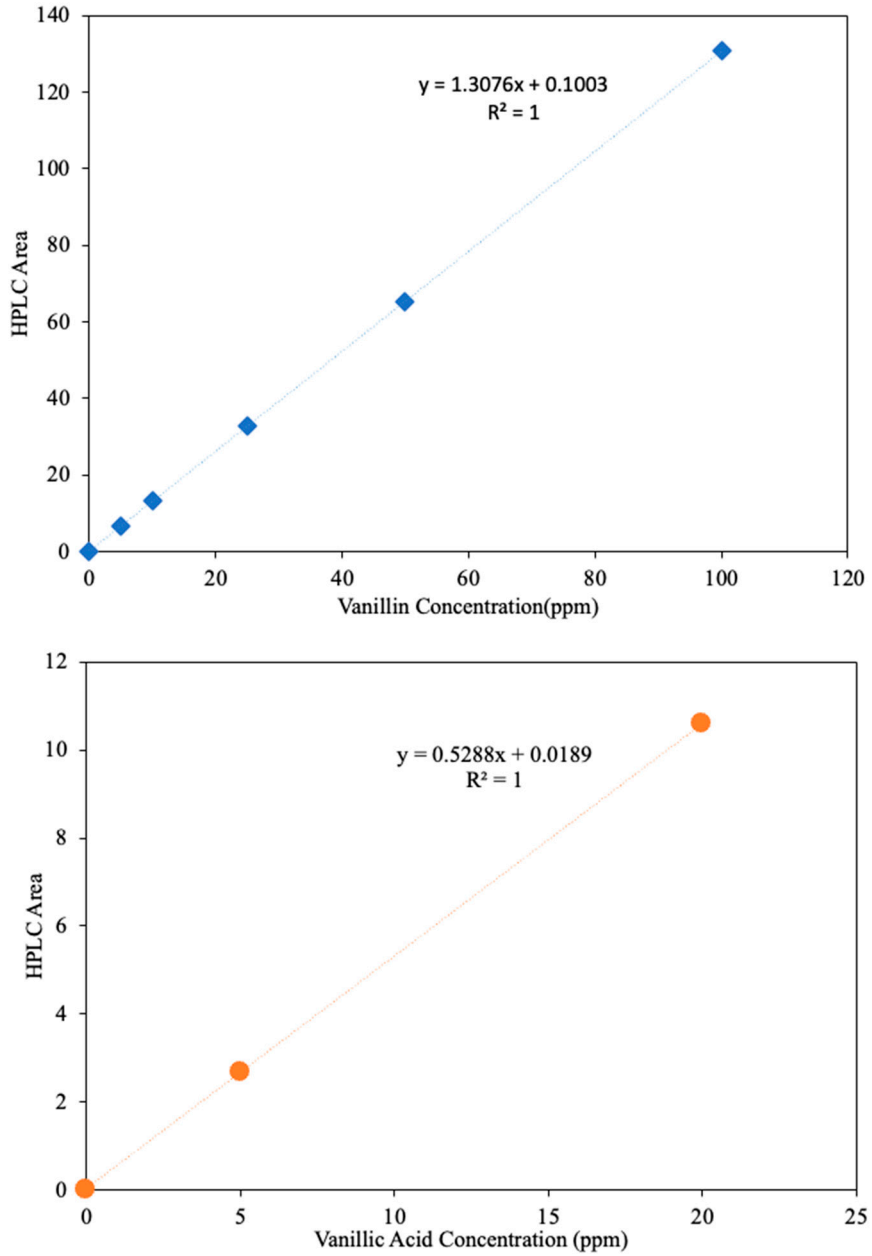

Figure S5. Vanillin and Vanillic Acid calibration curve for HPLC-UV

HPLC Chromatogram

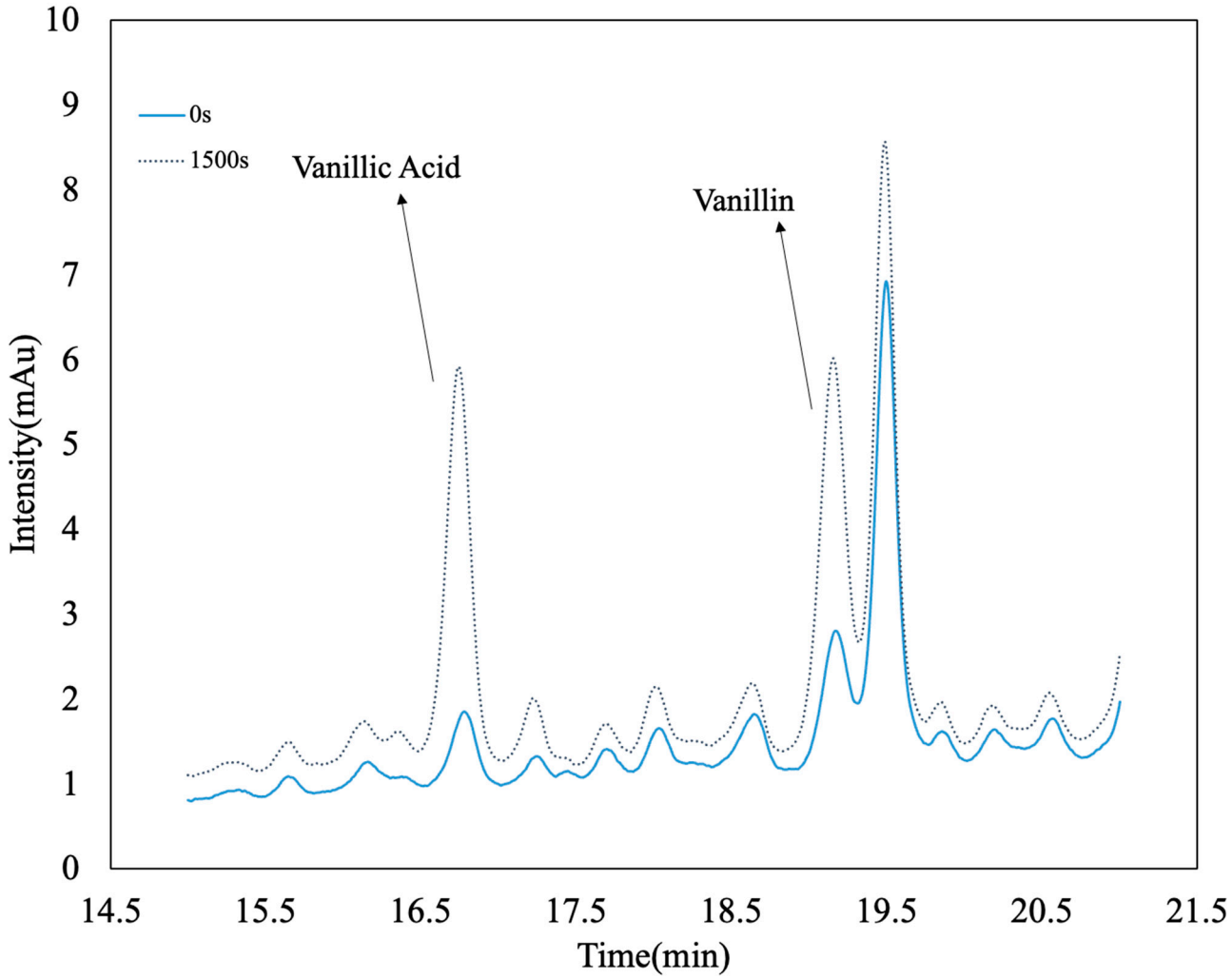

Figure S6. HPLC chromatogram for 200 nm Ni catalyst with 1 V applied voltage after 0 s and 1500 s

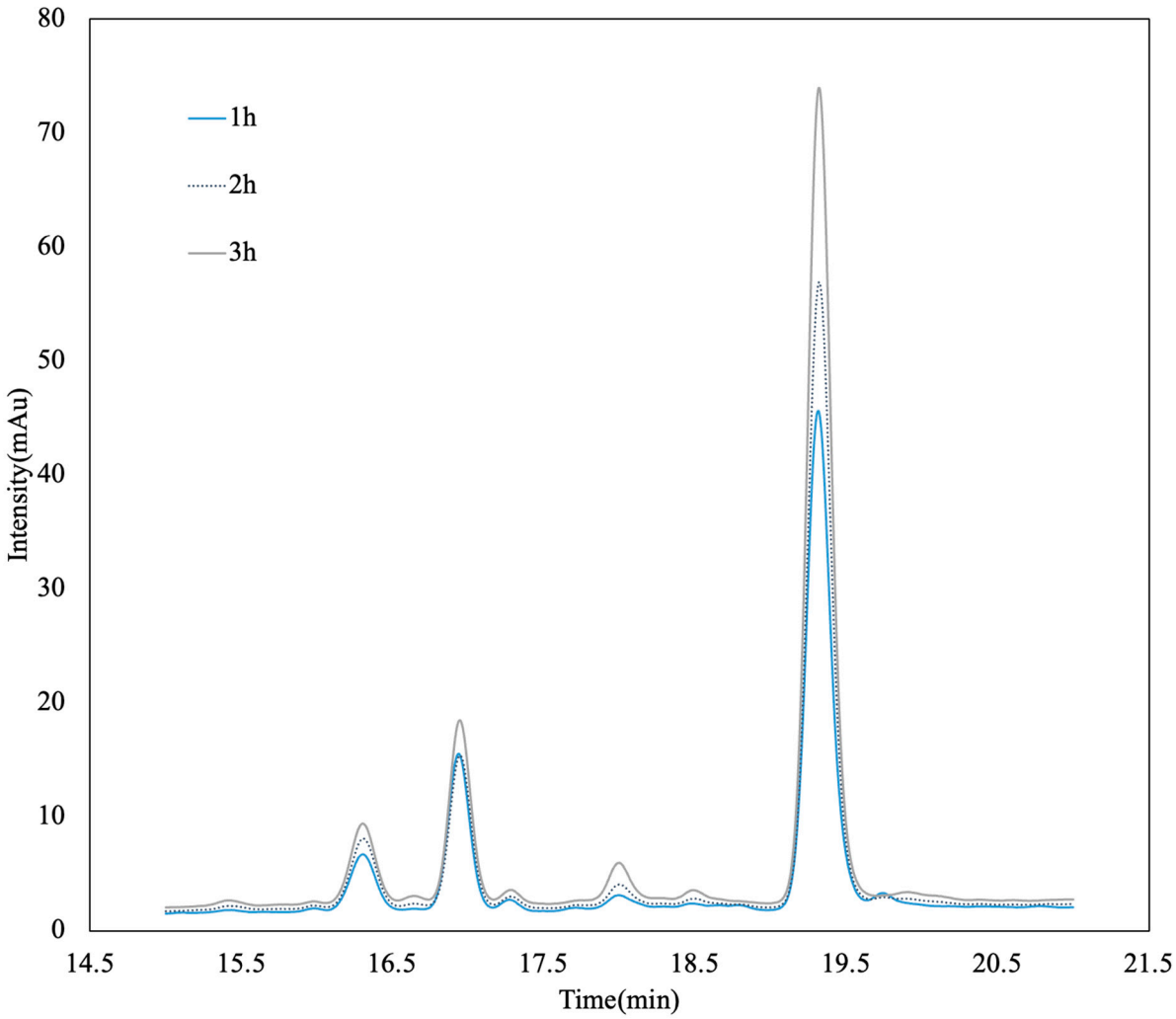

Figure S7. HPLC chromatogram for Ni foam catalyst with 1V applied voltage after 1 hour, 2 hours and 3 hours reaction.

ECSA

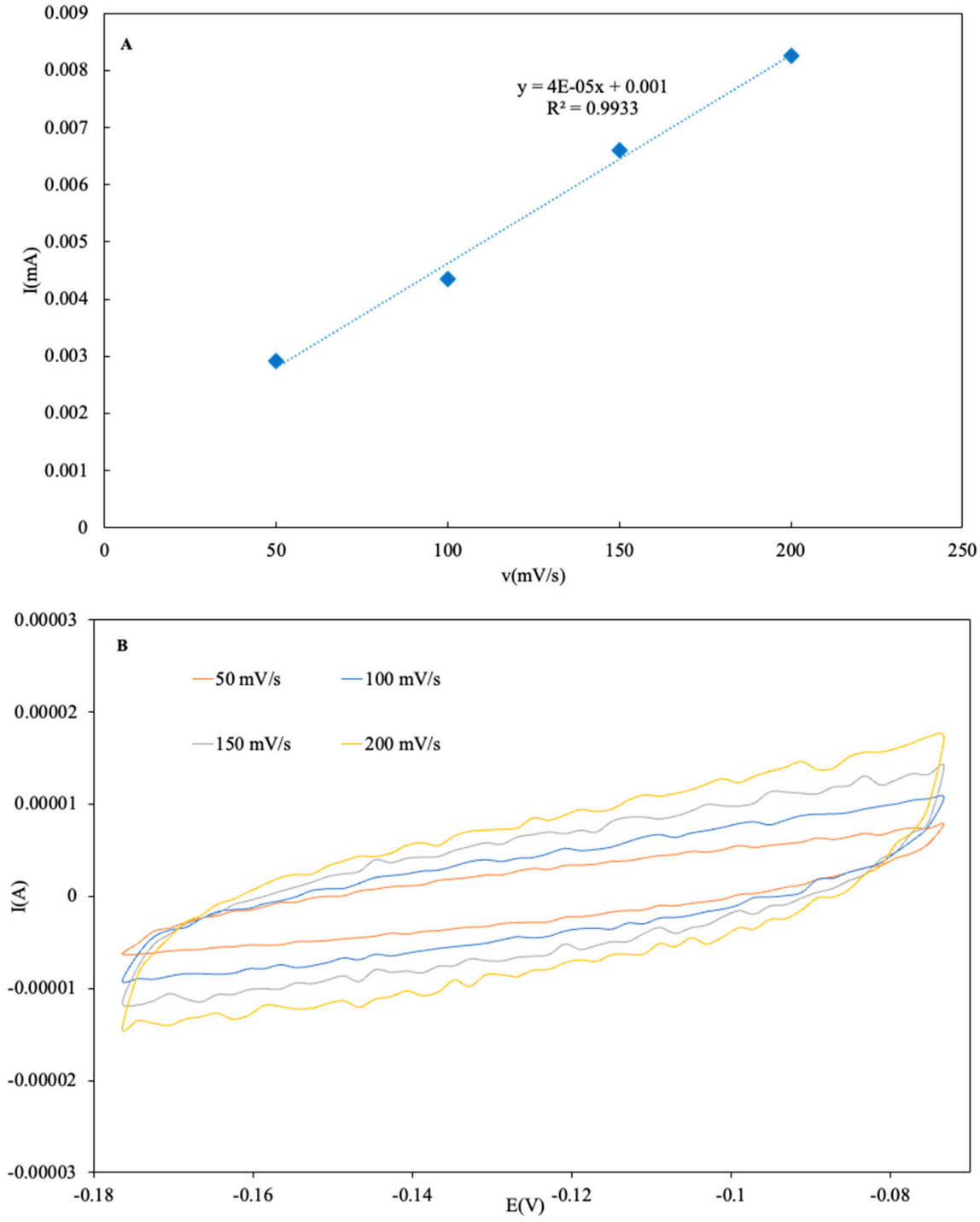

Figure S8. A: Double-layer capacitance plot for 100 nm Ni B: ECSA scans for 100 nm Ni

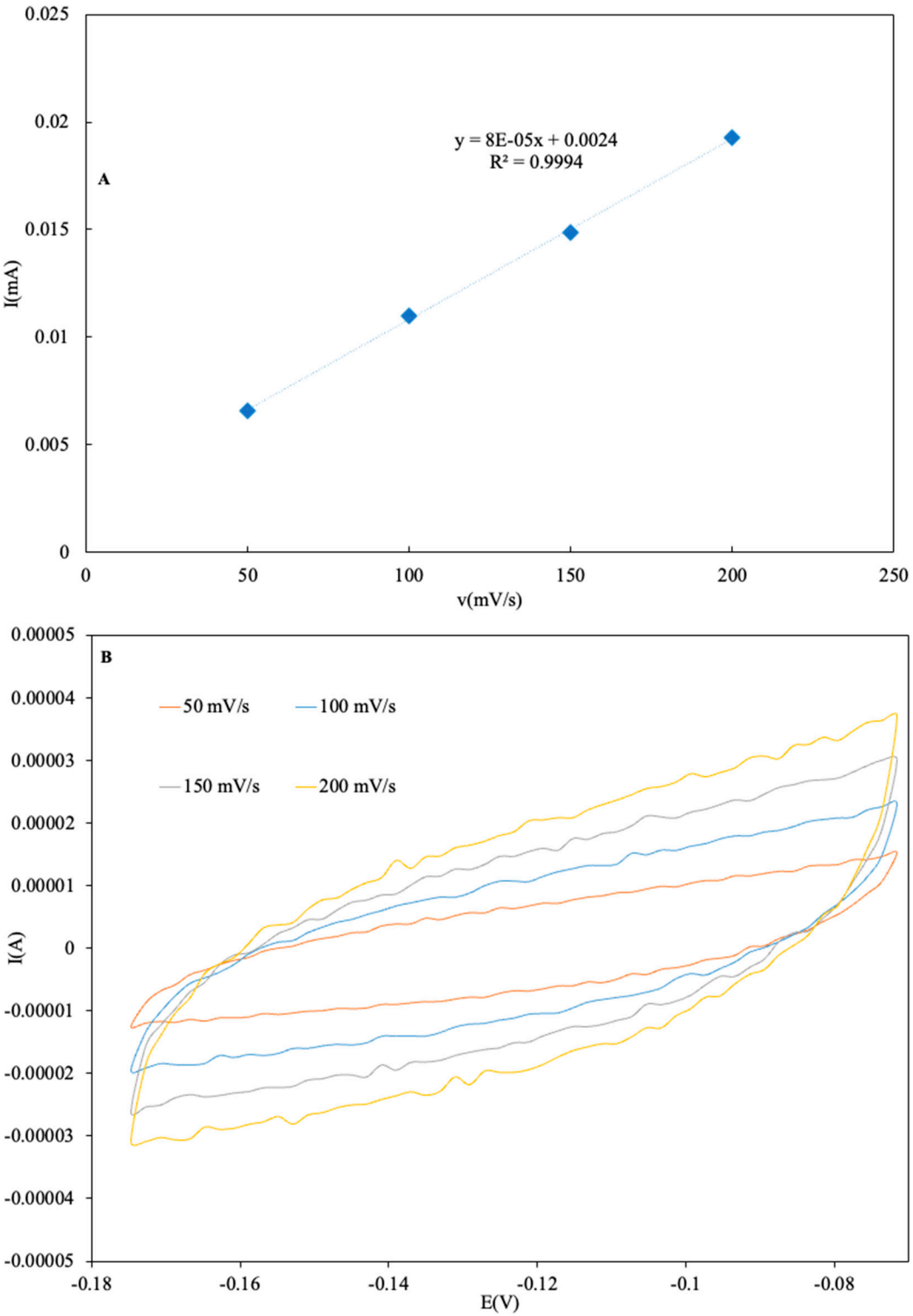

Figure S9. A: Double-layer capacitance plot for 200 nm Ni B: ECSA scans for 200 nm Ni

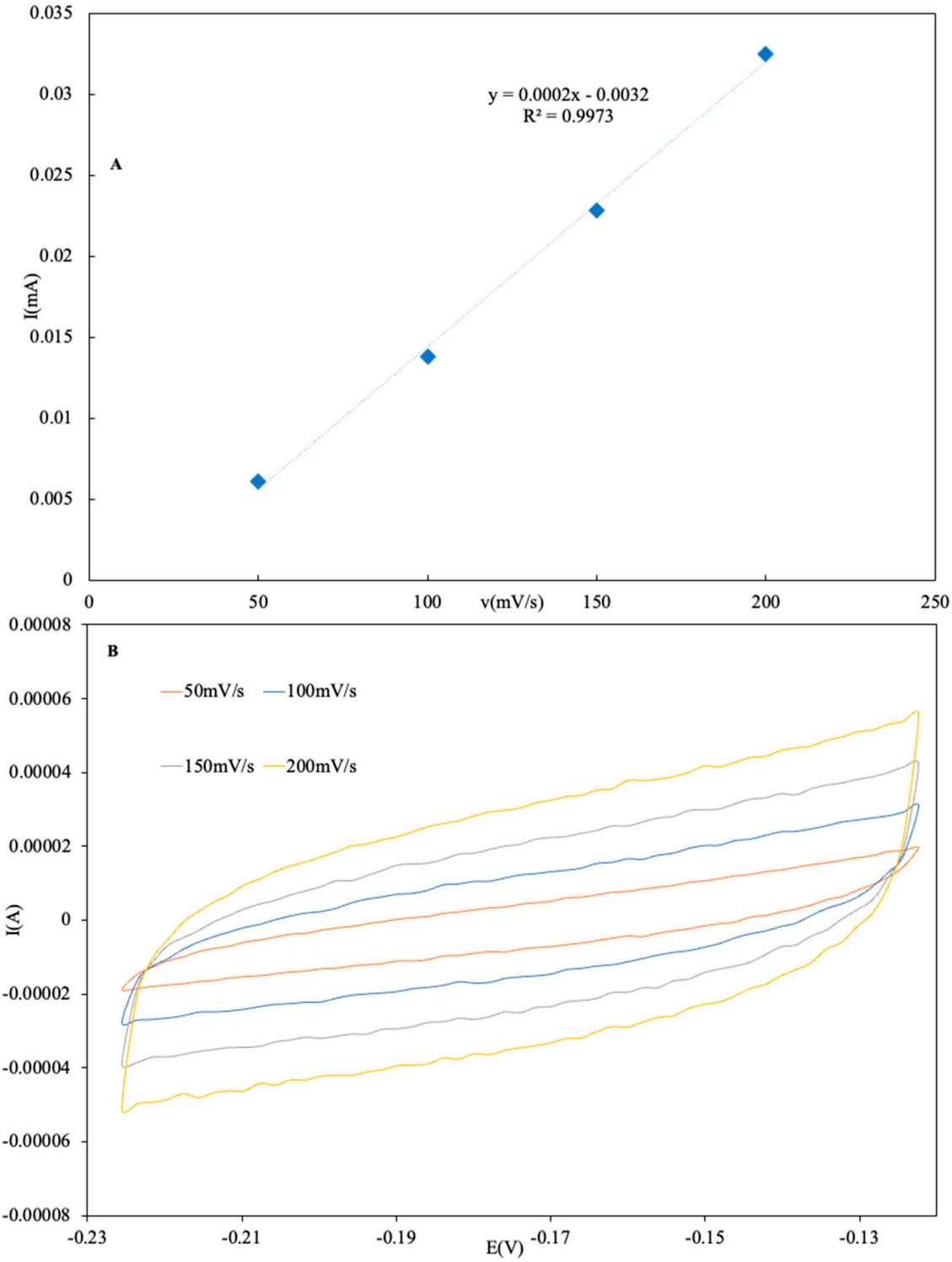

Figure S10. A: Double-layer capacitance plot for Ni foam B: ECSA scans for Ni foam