

Supplementary Materials

A rapid electrochemical method to recycle carbon fiber

composites using methyl radicals

Zehan Yu, ^{a,c} Y. Justin Lim, ^{b,c} Travis Williams, ^{b,*} and Steven Nutt ^{a,*}

^a *Department of Chemical Engineering and Materials Science, University of Southern California*

^b *Loker Hydrocarbon Research Institute, Wrigley Institute for Environment and Sustainability, and Department of Chemistry, University of Southern California*

^c *Co-first Author*

**Co-Corresponding Author: travisw@usc.edu*

**Co-Corresponding Author: nutt@usc.edu*

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1. General Procedures

All synthetic procedures were conducted in a chemical fume hood with exposure to air, unless otherwise indicated. Deuterated NMR solvents were purchased from Cambridge Isotopes Laboratories. 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) was supplied by Supelco. Unless otherwise specified, chloroform and all reagents (including sulfuryl chloride and AIBN) are commonly available from major commercial suppliers (Sigma-Aldrich, Merck, Fischer Scientific, TCI America, Acros Organics) and used without further purification. Dichloromethane, acetonitrile and hexanes are purchased from VWR and dried in a J. C. Meyer solvent purification system with alumina/copper (II) oxide columns; dichloromethane was dried by vacuum transfer from a calcium hydride suspension. Deionized water was purified in-house using a deionizer cartridge (Philadelphia Scientific).

NMR spectra were recorded on a Varian Mercury 400, Varian VNMRS 500, or VNMRS 600, spectrometers processed using MestReNova. All chemical shifts are reported in units of ppm and referenced to the residual ^1H or ^{13}C solvent peak and line-listed according to (s) singlet, (bs) broad singlet, (d) doublet, (t) triplet, (dd) double doublet, etc. ^{13}C spectra are delimited by carbon peaks, not carbon count. Air-sensitive NMR spectra were taken in 8" J-Young tubes (Wilmad or Norell) with Teflon valve plugs. Mass spectral data were acquired on an Agilent 6545 LC-QTOF instrument with electrospray set to positive ionization.

Pre-impregnated resin-fiber substrate materials, "prepregs" were fabricated in house or sourced from Solvay according to specified procedures. Cured CRFP panels were cut with a water jet cutter (ProtoMAX) as described.

Electrolysis was mediated with a Hanmatek HM310P potentiostat using the reactor described below and pictured in Figure 1 of the main text.

Images were recorded using a digital stereo microscope (Kenyence VHX-5000). SEM images were taken on a Helios G4 FIB/SEM (Thermo Scientific). EDS spectra were recorded on the Helios G4 FIB/SEM using Oxford UltimMax 170 Silicon Drift detector.

2. Electrolysis digestion experiment procedures:

a. Preparation of fully cured amine-epoxy CFRPs:

Epoxy equivalent weight (EEW) and amine hydrogen equivalent weight (AHEW) were used to calculate the mixing ratio of amine/epoxy. A resin of CFRP-A was formulated using the bifunctional epoxy diglycidyl ether of bisphenol A (17.95 g, EEW = 187 g/eq, Araldite GY 6010, Huntsman) and tetra-functional amine curing agent (6.05 g, 3,3'-diaminodiphenyl sulfone, AHEW = 63 g/eq, Aradur 9719-1, Huntsman). The mixing ratio of amine/epoxy was 100% (molar). After hand mixing epoxy and amine for 10 mins, the mixture was transferred into a vacuum oven (set at 120 °C) to vacuum degassing. After 10 mins, the mixture became clear and homogenous. A resin film was then prepared by spreading liquid resin onto a 203 x 203 mm release film (Airtech, Release Ease 236 TFNP), preheating at 50 °C on Wabash hot press. Prepreg was fabricated using 2 X 2 twill weave CF fabrics (FiberGlast 1069-B). One resin film was attached to each side of the CF fabric. Then, the stack was heated and pressed using a hot press at 50 °C with 20 kPa pressure for 1 min. CFRP-A panels were then laminated via a vacuum bag-only process (VBO) using 4 plies of prepreg. The curing cycle was (1) 1.5 °C /min to 120 °C, (2) hold at 120 °C for 3 hrs, (3) 1.5 °C/min to 180 °C and (4) hold at 180 °C for 3 hrs. Fully cured CFRP-A panels were then cut to 50.8 x 10.2 mm using a water-jet cutter.

CFRP-B panels were fabricated using 4 plies of aerospace-grade VBO prepreg (Solvay CYCOM 5320-1, T650, PW). The cure cycle was (1) hold at 60 °C for 2 hrs, (2) 1 °C/min to 120 °C, (2) hold at 120 °C for 2 hrs, (3) 1.7 °C/min to 177 °C, and (4) hold at 177 at 120 °C for 2 hrs. Fully cured CFRP-B panels were cut into 50.8 x 10.2 mm or 76.2 x 38.1 mm samples on a water-jet cutter.

b. Electrolysis digestion experiments

A CFRP sample was clamped by a PTFE (Teflon) platinum electrode holder and connected to a DC potentiostat as an anode, while a graphite rod served as the cathode as pictured in the main text and diagramed in Figure S1. The electrodes were immersed in the electrolyte solution containing CH₃COOH, NaCl, and DI water, according to loading details that are listed in Table 1 of the main text. For a 50.8 x 10.2 mm CFRP samples, 38.1 mm of the sample was immersed in solution and electrolyzed. Electrolysis reactions were performed in 180 mL electrolyte, using a 200 mL 5-neck glass vessel at reflux. For 76.2 x 38.1 mm CFRP samples, 44.4 mm of the sample was immersed in solution and electrolyzed. Electrolysis reactions were conducted in 250 mL electrolyte, using a 250 ml 4-neck glass vessel with a removal lid at reflux.

After electrolysis, reacted CF weaves of CFRP samples were cut using scissors. Then, the CF weaves were cleaned using water and acetone to remove excess reactants. CFRP-B samples were additionally washed by dimethyl sulfoxide (DMSO) to remove polyether sulfone hardener. Cleaned CFs fabrics were then dried at 130°C overnight in a convection oven.

Table S1: Electrolysis CFRP digestion experiment electrolyte summary

| Entry | CH ₃ COOH (ml, mol) | CH ₃ COOH (M) | NaCl (g, mol) | NaCl (M) | DI water(ml) |
|-------|--------------------------------|--------------------------|---------------|----------|--------------|
| 1 | 20, 0.35 | 1.93 | 10.52, 0.18 | 1 | 160 |
| 2 | 45, 0.78 | 4.35 | 10.52, 0.18 | 1 | 135 |
| 3 | 70, 1.22 | 6.77 | 10.52, 0.18 | 1 | 110 |
| 4 | 90, 1.57 | 8.70 | 10.52, 0.18 | 1 | 90 |
| 5 | 120, 2.09 | 11.6 | 10.52, 0.18 | 1 | 60 |
| 6 | 120, 2.09 | 11.6 | 7.89, 0.14 | 0.75 | 60 |
| 7 | 120, 2.09 | 11.6 | 5.26, 0.09 | 0.5 | 60 |
| 8 | 120, 2.09 | 11.6 | 10.52, 0.18 | 1 | 60 |
| 9 | 167, 2.91 | 11.6 | 14.61, 0.25 | 1 | 83 |

c. Remanufactured CFRPs using recovered CFs

Recovered CF weaves (44.4 x 38.1 mm) and in-house formulated resin were used to remanufacture CFRPs. Loose fibers were removed or organized from the recovered weaves. Then, a layer of resin was applied to the recovered CF fabric using a brush, and a new ply of CF weaves is placed on top. The process was repeated for all 4 plies in the laminate. Then, the stack was cured via a VBO process using the same curing cycle as the CFRP-A sample.

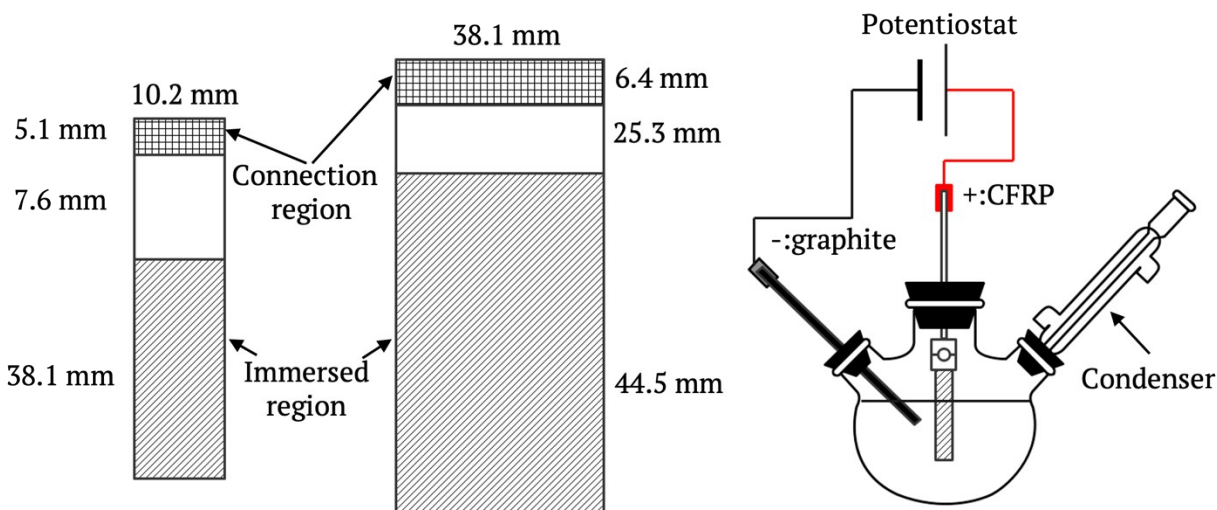


Figure S1: (a) CFRP samples 50.8 x 10.2 mm, (b) 76.2 x 38.1 mm, and (c) schematic of electrolysis recycling setup

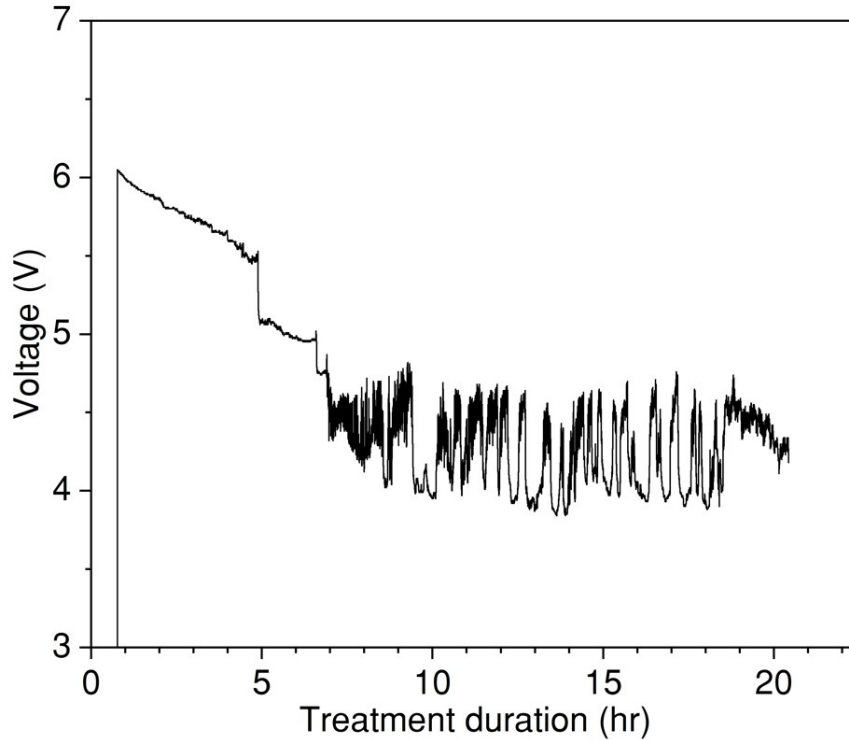


Figure S2: Measured voltage of Table 1, entry 5 (main text) during the electrolysis digestion

3. Single fiber tensile tests of virgin and electrolysis recycled CFs

CFRPs were laminated using 2 x 2 twill weave CF fabrics (FiberGlast 1069-B), and Solvay CYCOM 5320-1 resin films. Fully cured panels were cut into 79.25 x 10.16 mm samples. CFRP samples were electrolyzed in 200ml electrolyte (11.6M CH₃COOH, 1M NaCl) at 110°C for 20hrs. Recovered CFs were cleaned using DI water, acetone, and DMSO. Cleaned CFs were dried in a convection oven at 120°C overnight before testing.

The tensile properties of electrolysis-recycled CFs, and virgin fibers were tested and summarized in Table S2. A total of 44 tests were conducted, with 22 tests performed separately on the virgin and recycled CFs, following the IOS 11566 standard. The tensile strength for the fresh and electrolysis-recycled CFs were 2976.02 MPa and 2804.72 MPa. The modulus for the fresh and electrolysis-recycled CFs were 178.59 GPa and 149.01 GPa. Electrolysis-recycled CFs retained 94.24% of tensile strength and 83.43% of modulus.

Table S2: Single fiber tensile test summary of fresh and electrolysis-recycled CFs

| Samples | Break Force(N) | STDEV | Strength (MPa) | STDEV | Modulus (GPa) | STDEV |
|---------------------------|-----------------------|--------------|-----------------------|--------------|----------------------|--------------|
| Fresh CFs | 0.1340 | 0.0265 | 2976.02 | 592.62 | 178.59 | 18.84 |
| Electrolysis-recycled CFs | 0.1266 | 0.0282 | 2804.72 | 644.30 | 149.01 | 19.68 |
| Retention (%) | 94.48 | | 94.24 | | 83.43 | |

Sample mounting sheets were cut from printer paper into 25.4 x 76.2 mm strips with a 15.24 x 20.32 mm window in the center. Single fibers were separated from tows and mounted across the window of the mounting papers. Both sides of single fibers were affixed using double-sided tapes and epoxy adhesive (Henkel E-120HP) to secure the fibers in place.

Once the epoxy adhesive had cured, the mounted samples were examined using a light microscope (Keyence VHX-5000) using a 1000X lens to measure fiber diameter. The diameter of each sample was measured three times, and the resulting measured values were averaged to obtain the final measurement.

After mounting the sample onto the load frame, a cut was made in the center of the mounting sheet to free the fiber for testing. The samples were tested at 2mm/min crosshead speed till break. A total of 44 tests were conducted, with 22 tests performed on fresh CFs and another 22 tests on electrolysis-recycled CFs.

The CF cross-sections were assumed to be circular, and the areas were calculated using the diameters previously measured on the light microscope. The tensile strength was then calculated and plotted against strain (%) using these calculated areas. The slope of stress-strain curves was taken as tensile modulus. Table S3-4 summarize all tensile test results.

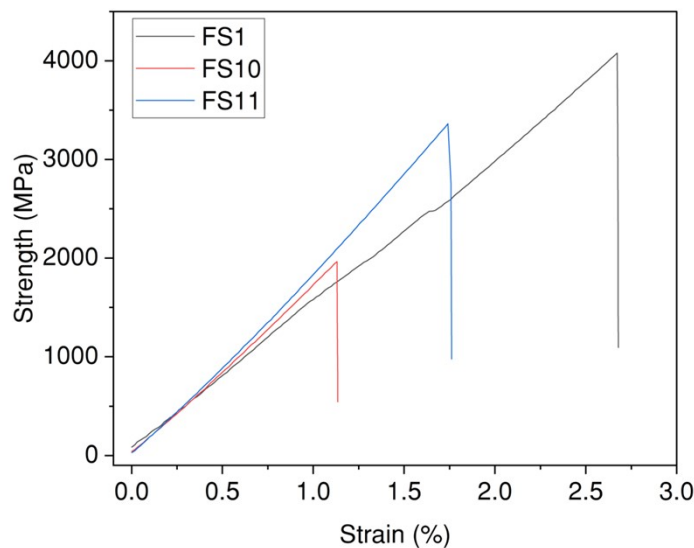


Figure S3: Representative stress-strain curves from tensile tests on fresh CF

Comment [SN]: Increase line weights on curves

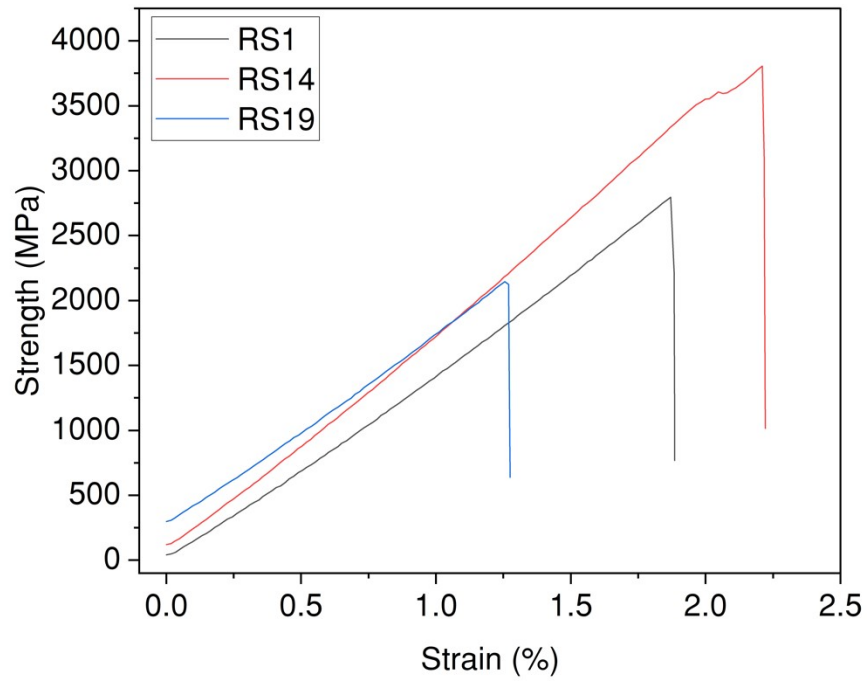


Figure S4: Representative stress-strain curves from tensile tests on electrolysis-recycled CF

Table S3: Summary of fresh CFs tensile tests

| Sample | Break Force (N) | Diameter (μm) | Tensile Strength (MPa) | Modulus (GPa) |
|--------|-----------------|----------------------------|------------------------|---------------|
| FS1 | 0.1785 | 7.5 | 4078.87 | 146.78 |
| FS2 | 0.1092 | 7.4 | 2516.44 | 159.02 |
| FS3 | 0.1264 | 7.6 | 2811.68 | 160.84 |
| FS4 | 0.1757 | 7.6 | 3909.47 | 158.20 |
| FS5 | 0.1531 | 7.5 | 3467.91 | 165.10 |
| FS6 | 0.1164 | 7.5 | 2612.82 | 159.39 |
| FS7 | 0.0886 | 7.6 | 1937.90 | 154.97 |
| FS8 | 0.1497 | 7.5 | 3359.18 | 172.30 |
| FS9 | 0.1277 | 7.6 | 2815.74 | 185.45 |
| FS10 | 0.0876 | 7.5 | 1966.35 | 171.52 |
| FS11 | 0.1525 | 7.6 | 3363.14 | 192.72 |
| FS12 | 0.1364 | 7.6 | 3007.83 | 178.85 |
| FS13 | 0.1460 | 7.5 | 3306.44 | 213.58 |
| FS14 | 0.0994 | 7.5 | 2270.33 | 184.21 |
| FS15 | 0.1202 | 7.6 | 2673.51 | 189.06 |
| FS16 | 0.1628 | 7.7 | 3527.48 | 218.13 |
| FS17 | 0.1542 | 7.6 | 3400.41 | 191.06 |
| FS18 | 0.1681 | 7.6 | 3675.98 | 198.58 |
| FS19 | 0.1245 | 7.6 | 2770.51 | 191.79 |
| FS20 | 0.1070 | 7.8 | 2258.61 | 185.06 |
| FS21 | 0.1355 | 7.7 | 2911.09 | 166.94 |
| FS22 | 0.1295 | 7.6 | 2830.77 | 185.49 |
| AVG | 0.1340 | 7.6 | 2976.02 | 178.59 |
| STDEV | 0.0265 | 0.1 | 592.62 | 18.84 |

Table S4: Summary of electrolysis-recycled CFs tensile tests

| Sample | Break Force (N) | Diameter (μm) | Tensile Strength (MPa) | Modulus (GPa) |
|--------|-----------------|----------------------------|------------------------|---------------|
| RS1 | 0.1246 | 7.5 | 2797.11 | 149.10 |
| RS2 | 0.0849 | 7.8 | 1776.82 | 115.45 |
| RS3 | 0.1073 | 7.6 | 2366.48 | 140.73 |
| RS4 | 0.1076 | 7.6 | 2404.63 | 113.43 |
| RS5 | 0.0801 | 7.4 | 1846.24 | 137.32 |
| RS6 | 0.1081 | 7.9 | 2225.43 | 121.99 |
| RS7 | 0.0821 | 7.5 | 1859.31 | 116.35 |
| RS8 | 0.1320 | 7.6 | 2911.01 | 154.32 |
| RS9 | 0.1428 | 7.6 | 3149.43 | 164.05 |
| RS10 | 0.1652 | 7.5 | 3773.60 | 171.67 |
| RS11 | 0.1580 | 7.6 | 3485.54 | 172.44 |
| RS12 | 0.1310 | 7.7 | 2838.93 | 156.75 |
| RS13 | 0.1486 | 7.6 | 3249.00 | 162.49 |
| RS14 | 0.1726 | 7.6 | 3806.88 | 174.37 |
| RS15 | 0.1557 | 7.6 | 3464.25 | 174.66 |
| RS16 | 0.1452 | 7.5 | 3318.21 | 155.21 |
| RS17 | 0.1545 | 7.5 | 3468.04 | 162.21 |
| RS18 | 0.1392 | 7.5 | 3180.42 | 141.54 |
| RS19 | 0.0973 | 7.6 | 2145.71 | 148.85 |
| RS20 | 0.1359 | 7.6 | 2996.81 | 162.90 |
| RS21 | 0.1218 | 7.7 | 2639.76 | 153.38 |
| RS22 | 0.0915 | 7.6 | 2000.21 | 128.95 |
| AVG | 0.1266 | 7.6 | 2804.72 | 149.01 |
| STDEV | 0.0282 | 0.1 | 644.30 | 19.68 |

4. EDS images of the reclaimed carbon fiber surface

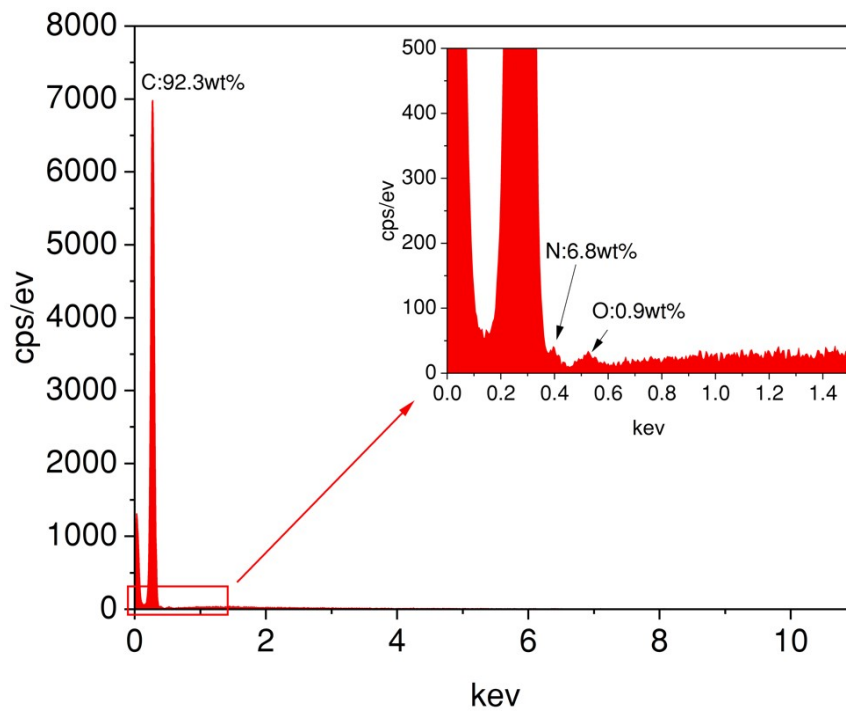


Figure S5: EDS spectrum of virgin CF

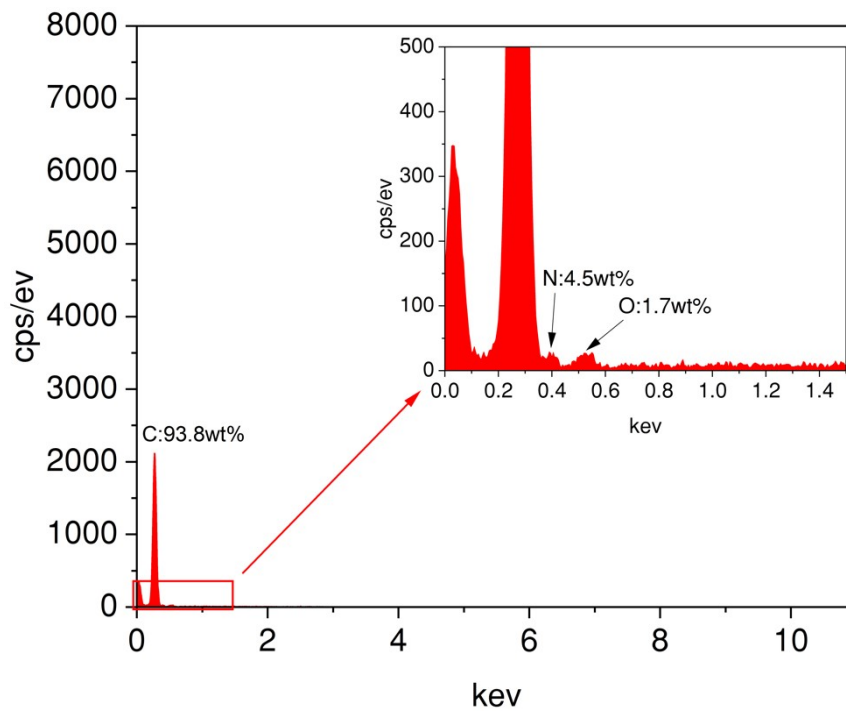


Figure S6: EDS spectrum of recycled CF from main text Table 1 entry 5

5. EPR spectrum of captured radicals in the electrolyzed system

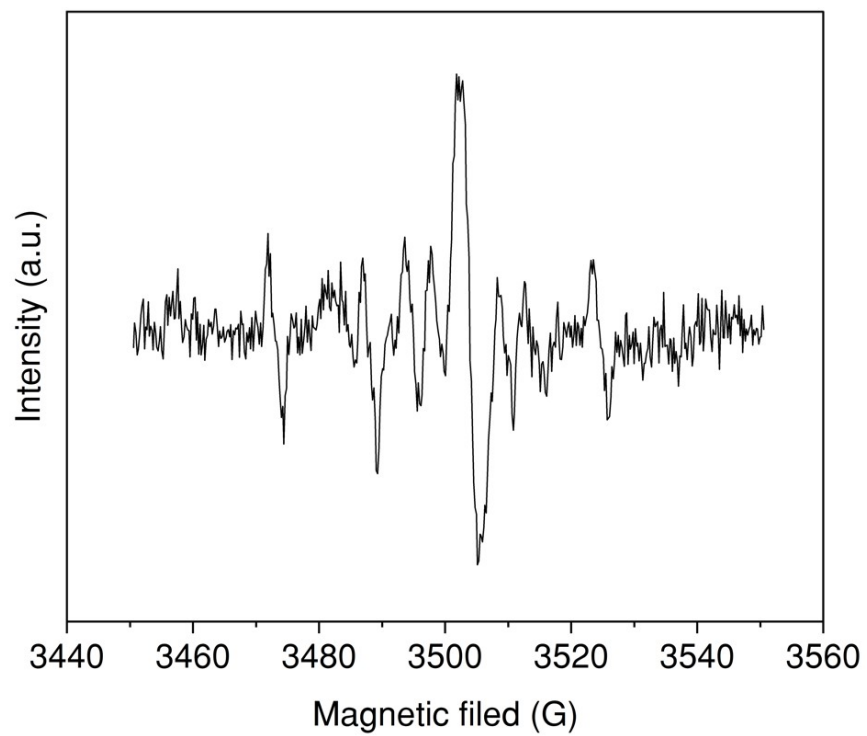


Figure S7: EPR spectrum of the product of Table 3, entry A1 (main text)

6. Supporting NMR spectrum for active radical detection experiments:

a. ^1H NMR spectrum of 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO)

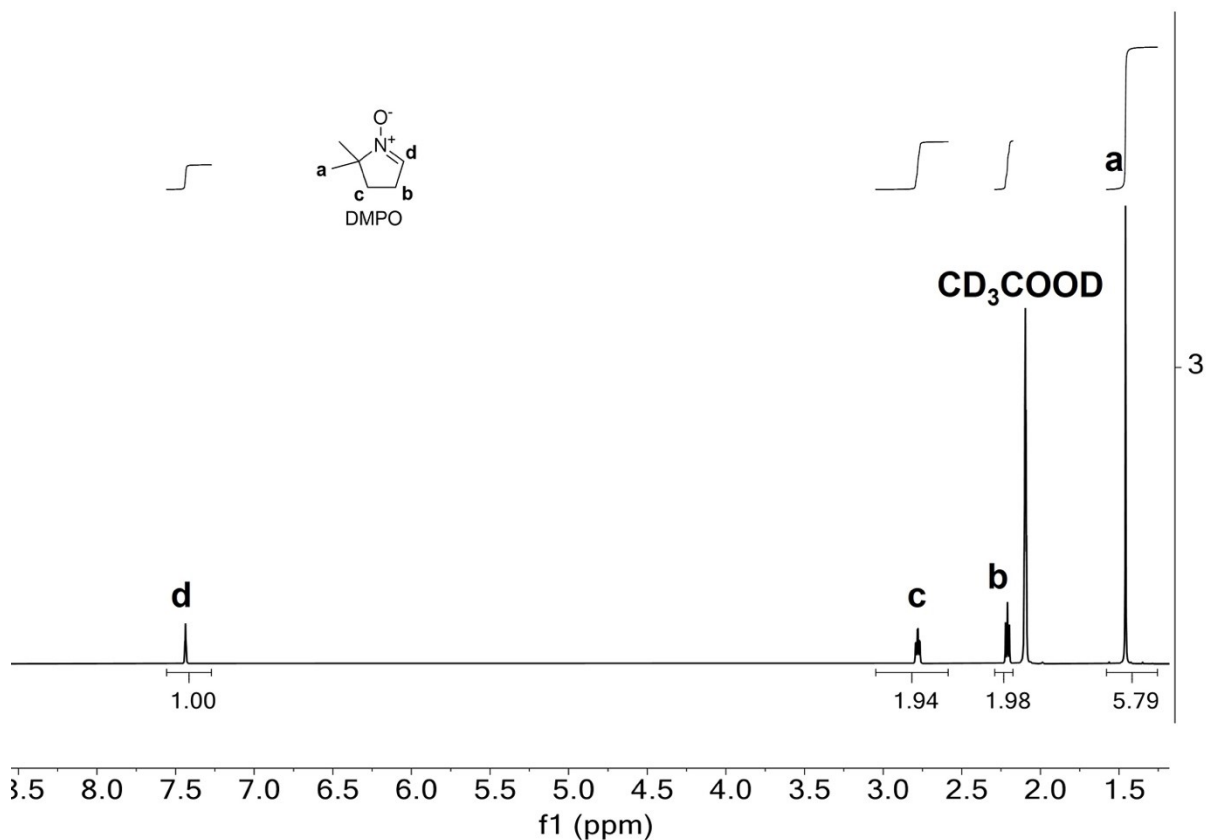


Figure S8: ^1H NMR spectrum of commercial DMPO

^1H NMR (600 MHz, acetic acid) δ 7.44 (t, $J = 2.5$ Hz, 1H), 2.78 (td, $J = 7.4, 2.5$ Hz, 2H), 2.21 (t, $J = 7.4$ Hz, 2H), 1.46 (s, 6H).

b. ^1H NMR stacked spectra of DMPO digestion in electrolyzed system

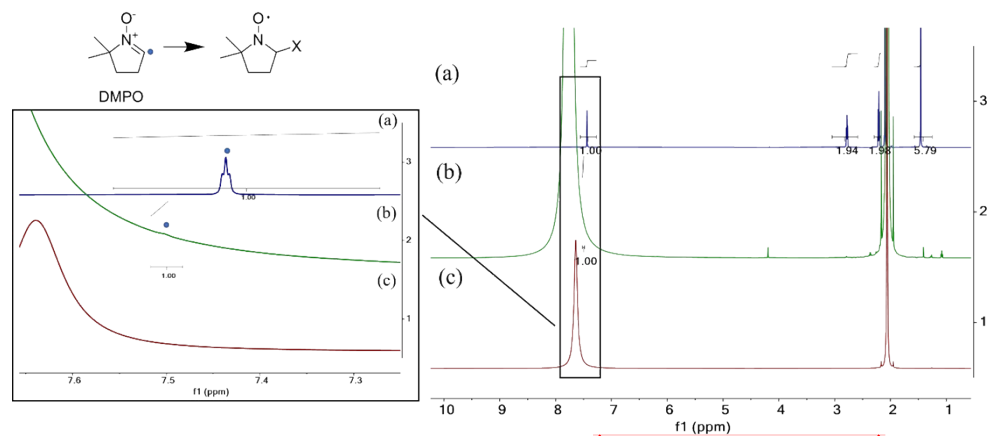


Figure S9: Stacked ^1H NMR spectrum of main text Table 3, entries A1 and A2

c. COSY spectra of products of Table 3 (A1 and A2)

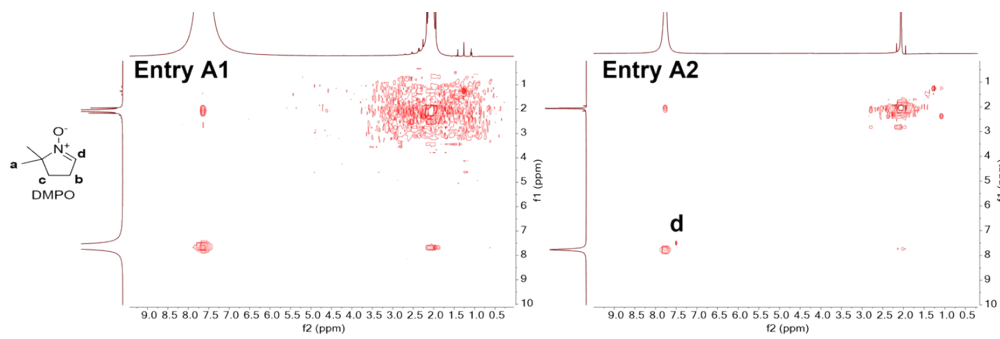


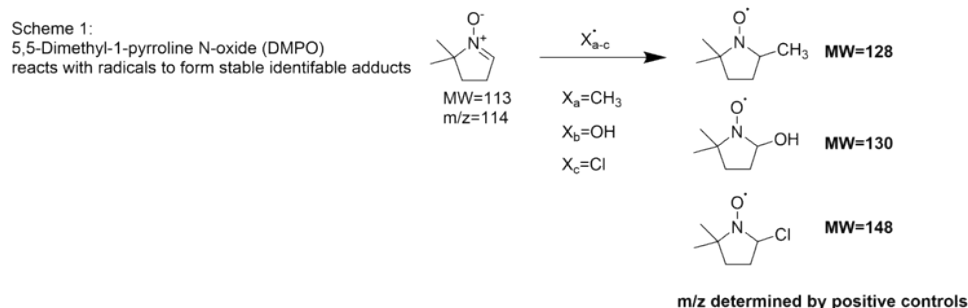
Figure S10: COSY NMR spectrum of main text Table 3, entries A1 and A2

Comment [SN]: Increase line weight on inset plot

7. Mass spectra from DMPO spin trap experiments

a. Main text Table 3, entry A1

In the 5-neck glass electrolysis vessel (main text scheme 2), acetic acid (10 mL, 17.4 M) and NaCl (876.6 mg, 1 M) were dissolved in deionized water (5 mL). The electrolysis apparatus was assembled as described above, and a voltage of 4 V was applied. The vessel was flushed with argon gas and allowed to react for 5 minutes. The solution was then heated to 65 °C and DMPO (15.0 mg, 31.3 μ mol, 8.84 mM) was added. A sample aliquot was collected after 60 minutes.



Scheme S1: Active radical trap experiment and identification protocol

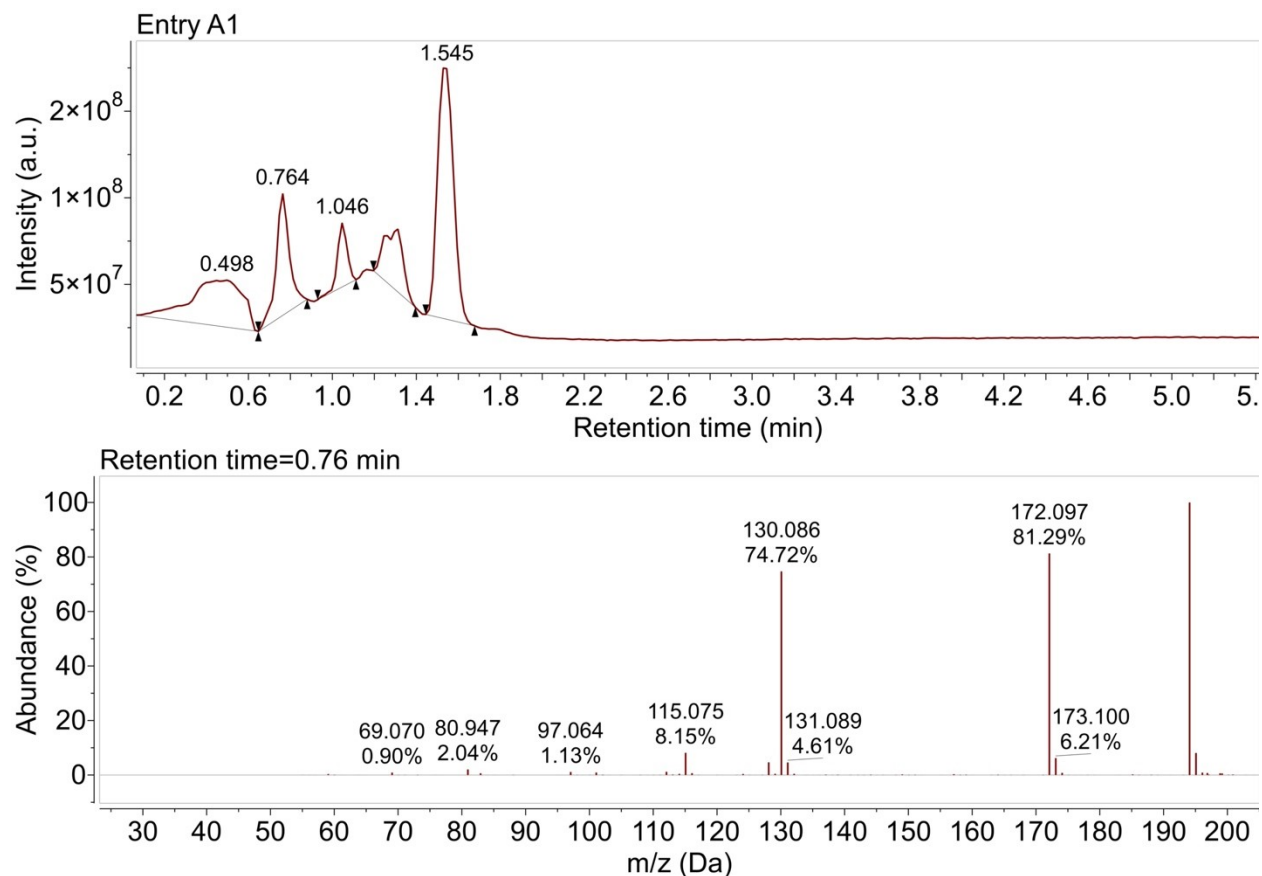
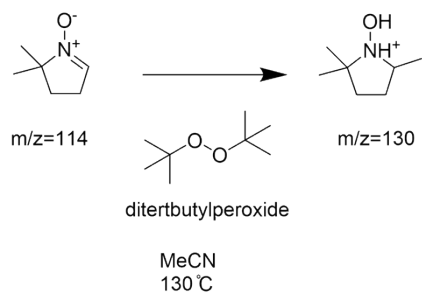


Figure S11: Mass spectrum of Table 3, entry A1(main text). MS profile for RT = 0.76 min

b. DMPO-Methyl adduct Positive Control

In a 5 mL oven dried round bottom flask were combined acetonitrile (1.0 mL) and di-tert-butylperoxide (7.0 mg, 38 μmol). The solution was heated to 130 $^{\circ}\text{C}$, then after two minutes DMPO (10 mg, 8.9 μmol) was added into the solution (8.85 mM). The resulting solution was heated for 1 hour before the heat was turned off.



Scheme S2: DMPO-methyl adduct positive control experiment

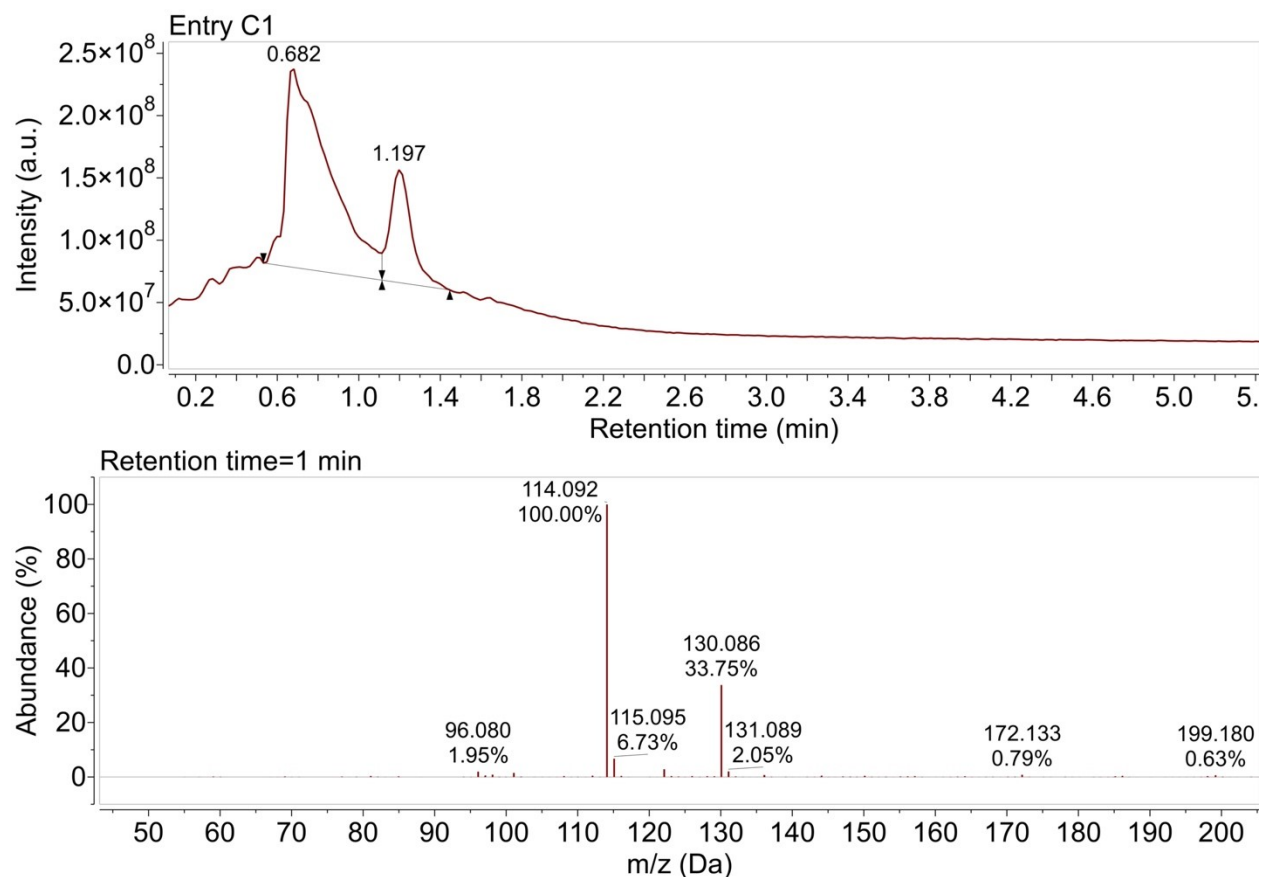
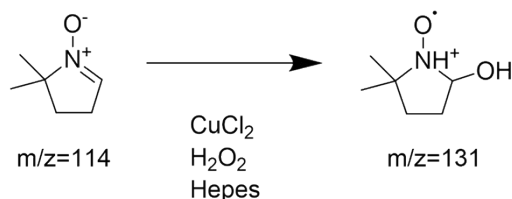


Figure S12: Mass spectrum of Table 4, entry C1 (main text). MS profile for RT = 1 min

c. DMPO-Hydroxyl adduct Positive Control

In a 10 mL oven dried round bottom flask were combined H₂O₂ (5.0 mL, 10 mM aq) and copper(II) chloride (400 μg, 3.0 μmol) to make [Cu] = 0.6 mM. Hepes buffer (Alfa Aesar), solid, 3.0 mg, to make 2.5 mM) was added into the solution. The resulting solution was stirred for two minutes at room temperature before DMPO (15 mg, 130 μmol, to make 27 mM) was added. An aliquot was recovered for analysis after 45 minutes.



Scheme S3: DMPO-hydroxyl adduct positive control experiment

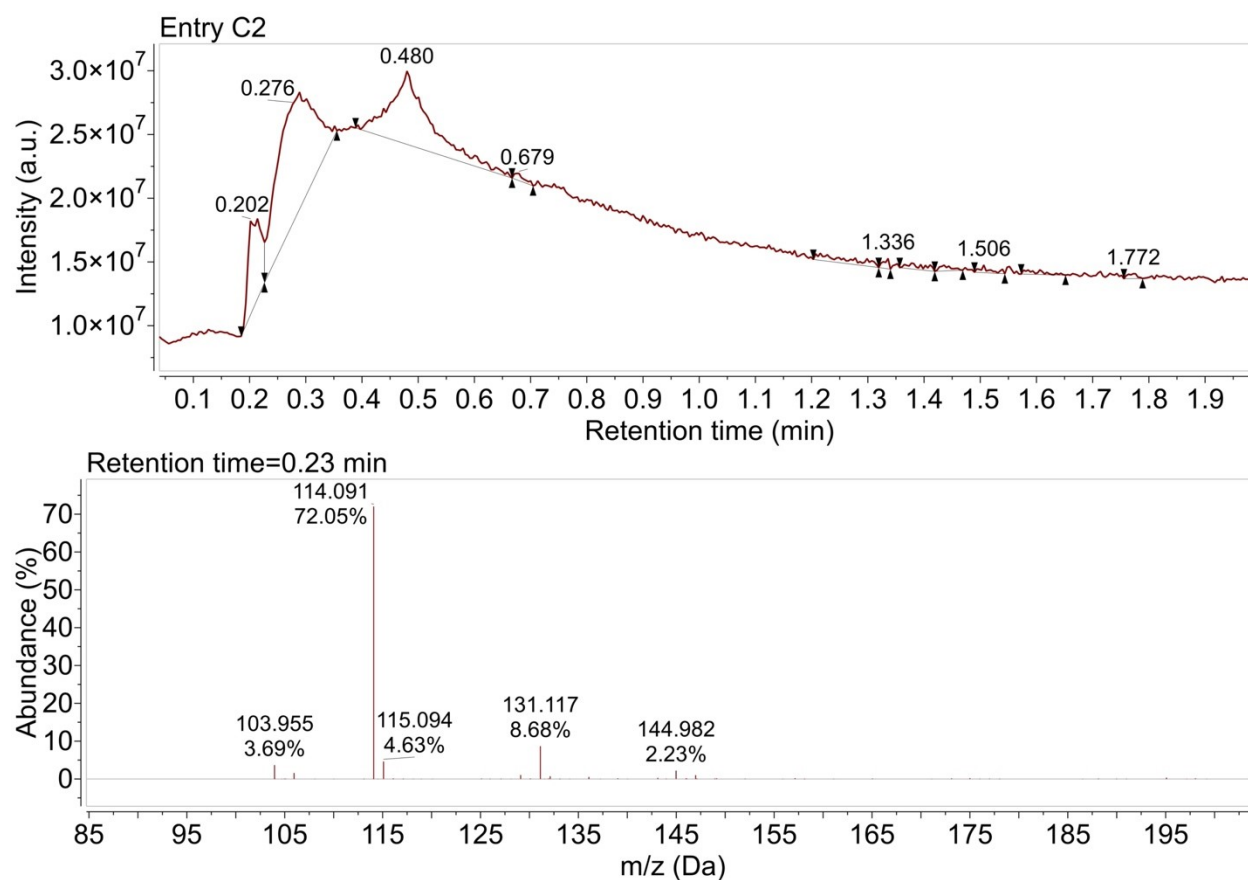
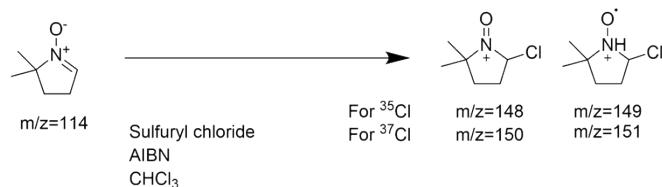


Figure S13: Mass spectrum of Table 4, entry C2(main text). MS profile for RT=0.23 min

d. DMPO-Chlorine adduct Positive Control

In a 25 mL oven dried round bottom flask were combined chloroform (10 mL), sulfuryl chloride (2.0 mL, 25 mmol, 2.5 M), and azobisisobutyronitrile (AIBN, 10 mg, 61 μ mol). The vessel was purged with nitrogen gas, a condenser was attached, and the solution was heated to 55 $^{\circ}$ C. After two minutes DMPO (15 mg, 13 μ mol, 13 mM) was added. An aliquot was recovered for analysis after 20 minutes.



Scheme S4: DMPO-chlorine adduct positive control experiment

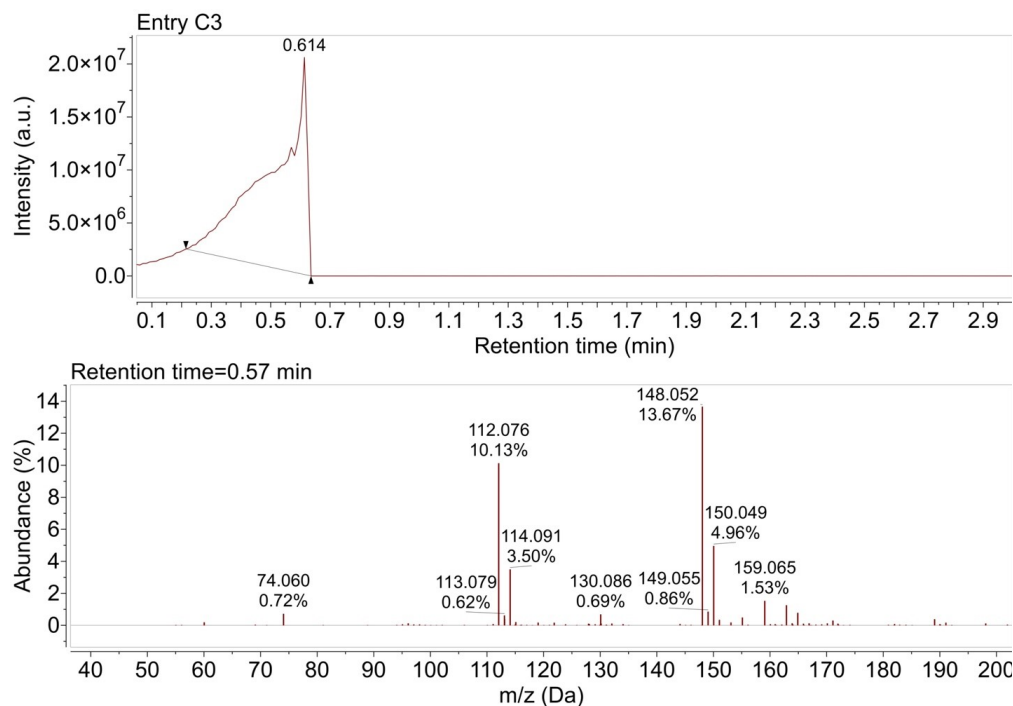


Figure S14: Mass spectrum of Table 4, entry C3 (main text). MS profile for RT=0.57 min.

Comment [SN]: Increase font sizes on plots

8. GC analysis of electrolysis headspace

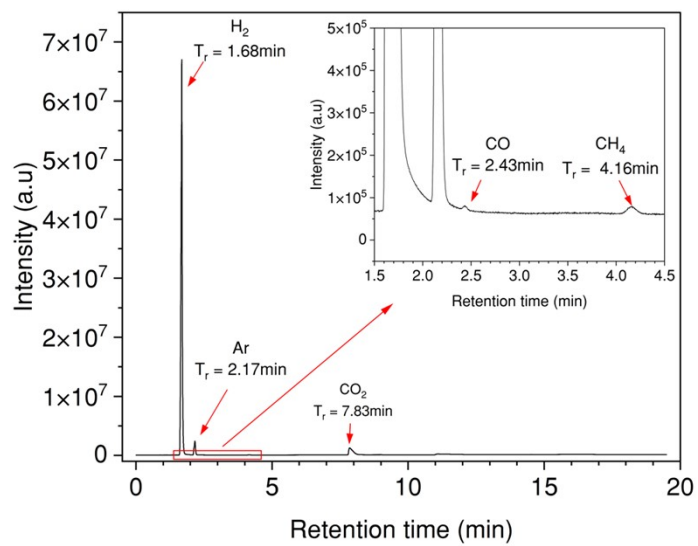


Figure S15: GC of electrolysis set-up headspace

Comment [SN]: Increase font size on plot annotations

9. Supporting NMR spectrum for active radical detection experiments:

a. ^1H NMR spectrum of 3,3'-sulfonylbis(*N,N*-dibutylaniline) (Bu_4DDS)

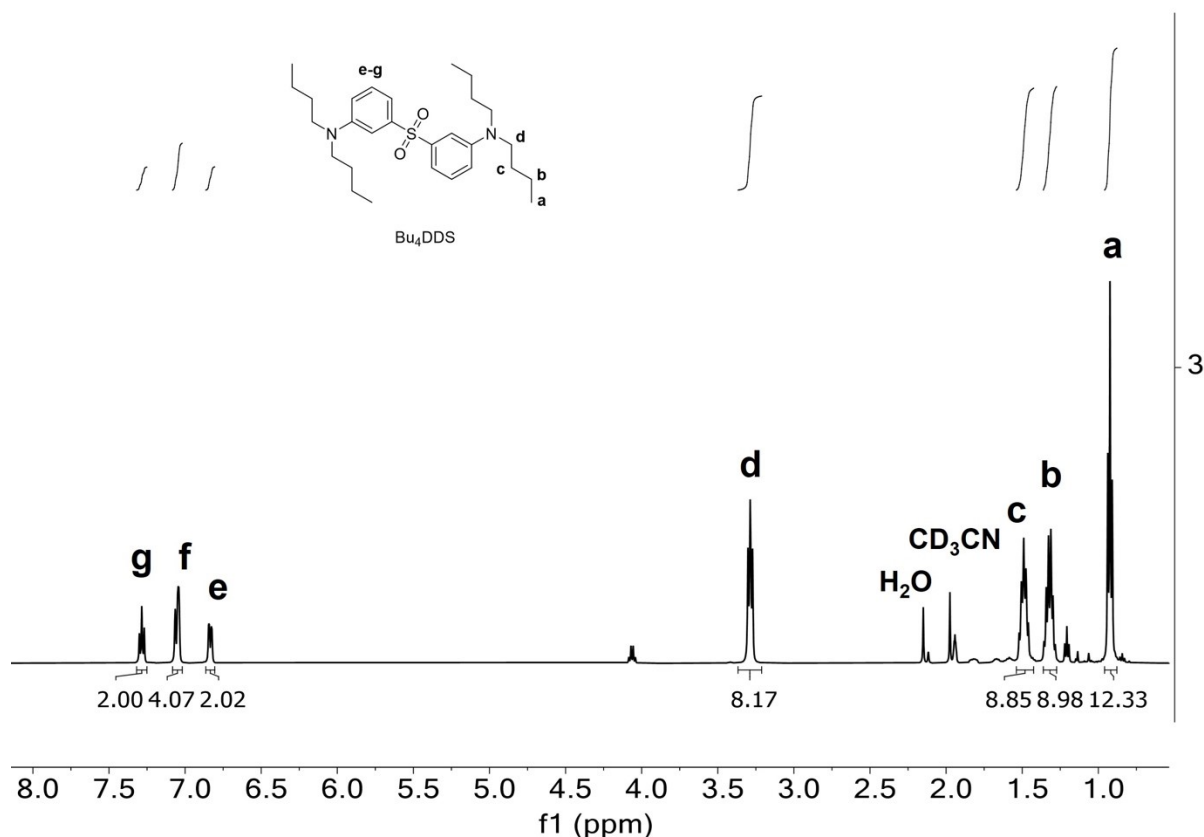


Figure S16: ^1H NMR spectrum of Bu_4DDS matrix model

^1H NMR (500 MHz, cd_3cn) δ 7.28 (t, J = 8.0 Hz, 2H), 7.08 – 7.02 (m, 4H), 6.83 (dd, J = 8.5, 2.7 Hz, 2H), 3.29 (t, J = 7.6 Hz, 8H), 1.49 (p, J = 7.6 Hz, 9H), 1.32 (h, J = 7.4 Hz, 9H), 0.92 (t, J = 7.4 Hz, 12H).

^{13}C NMR (100 MHz, cd_3cn) δ 148.49, 142.76, 130.08, 115.72, 112.74, 109.11, 50.25, 28.77, 19.84, 13.27.

FT-IR (thin film) ν = 1187 (C-N), 1497 (CH_2), 1597 (C=C), 1305, 1153 (S=O) cm^{-1} .

Q-TOF MS m/z = $\text{C}_{28}\text{H}_{44}\text{N}_2\text{O}_2\text{S}$, calculated mass 472, found protonated mass $[\text{C}_{28}\text{H}_{45}\text{N}_2\text{O}_2\text{S}]^{1+}$ 473.321 g/mol.

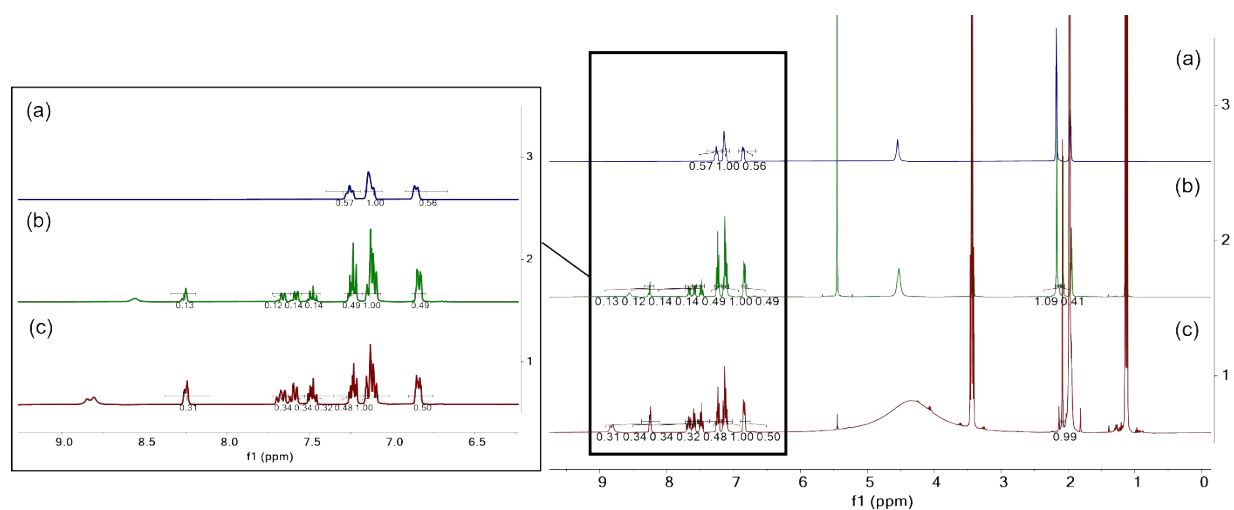
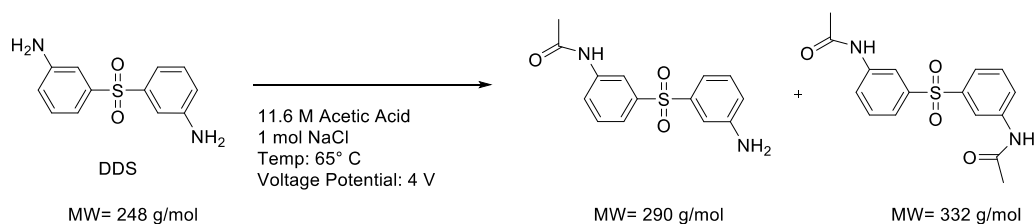


Figure S18: Stacked ^1H NMR spectra of (a) 3,3'-diaminodiphenylsulfone (DDS), DDS in electrolysis digestion conditions for (b) 1 hour (b), and (c) 5 hours

d. MS spectrum of DDS digestion in electrolyzed system for 1 hour



Scheme S5: Proposed DDS acylation reaction

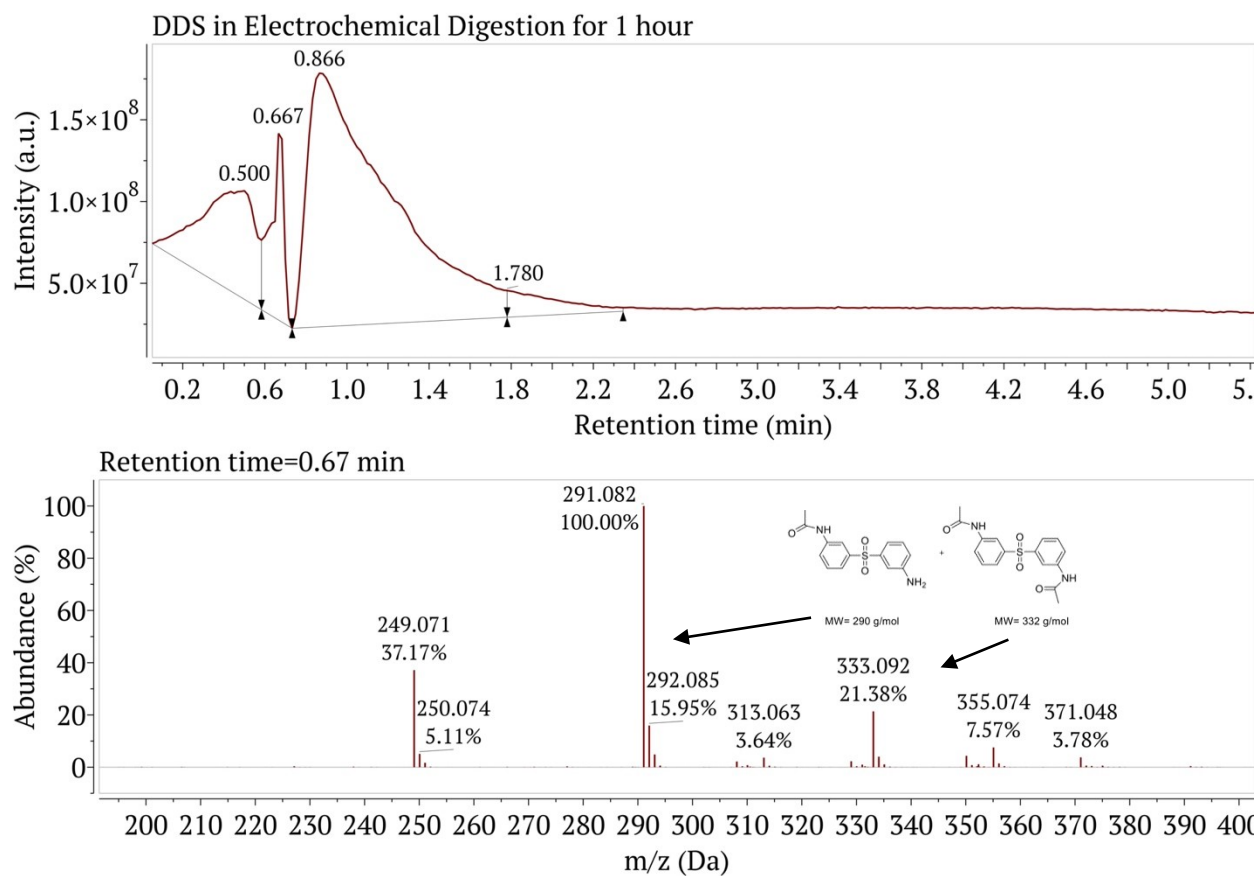


Figure S19: LC-QTOF mass profile of DDS in electrolysis digestion conditions for 1 hour.

The molecule DDS undergoes an acylation reaction with the solvent to form both the mono and bis amide.