Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary information for:

Speciation of potential dependent fouling on copper foil electrodes during electrochemical hydrogenation and hydrogenolysis of furfural in strong acid

Andrew S. May and Elizabeth J. Biddinger

Department of Chemical Engineering, The City College of New York, CUNY, New York, New York 10031, United States

Table S1. Reaction data for FF ECH at -560 mV RHE.

	t	X	MB	S FA	S MF	FE FA	FE MF
	min						
ECH1	0	0.000	1.000	0.000	0.000	0.000	0.000
	30	0.149	0.916	0.127	0.311	0.109	0.463
	60	0.241	0.867	0.130	0.312	0.102	0.467
	120	0.412	0.763	0.118	0.294	0.091	0.467
	180	0.601	0.659	0.116	0.296	0.076	0.438
ECH2	0	0.000	1.000	0.000	0.000	0.000	0.000
	30	0.102	0.959	0.193	0.494	0.107	0.464
	60	0.193	0.903	0.132	0.348	0.091	0.427
	120	0.345	0.815	0.099	0.346	0.072	0.479
	180	0.431	0.737	0.099	0.349	0.066	0.471
ECH3	0	0.000	1.000	0.000	0.000	0.000	0.000
	30	0.079	0.955	0.149	0.279	0.122	0.394
	60	0.115	0.931	0.145	0.266	0.112	0.404
	120	0.178	0.886	0.108	0.245	0.099	0.451
	180	0.207	0.829	0.094	0.276	0.082	0.470

Table S2. Reaction data for FF ECH at -700 mV RHE.

	t	X	MB	S FA	S MF	FE FA	FE MF
	min						
ECH1	0	0.000	1.000	0.000	0.000	0.000	0.000
	30	0.158	0.908	0.135	0.282	0.096	0.381
	60	0.268	0.830	0.130	0.230	0.100	0.381
	120	0.352	0.763	0.115	0.209	0.096	0.392
	180	0.434	0.721	0.101	0.228	0.081	0.386
ECH2	0	0.000	1.000	0.000	0.000	0.000	0.000
	30	0.102	0.927	0.103	0.170	0.125	0.356
	60	0.138	0.881	0.153	0.172	0.124	0.348
	120	0.189	0.845	0.144	0.164	0.123	0.350
	180	0.247	0.799	0.110	0.170	0.099	0.347
ECH3	0	0.000	1.000	0.000	0.000	0.000	0.000
	30	0.060	0.960	0.183	0.170	0.144	0.267
	60	0.126	0.913	0.179	0.178	0.137	0.322
	120	0.190	0.859	0.112	0.126	0.126	0.328
	180	0.234	0.816	0.098	0.157	0.104	0.347

Table S3. Assignment of primary bands seen in commercial pFA.

Wavenumber [cm^{-1}]	**Functionality and citations**
3417	O-H stretch [1, 2, 3]
3118	C-H stretch of ring [1, 3]
2922	Asymmetric CH_2 stretch [1, 3]
2848	Symmetric CH stretch [1]
1715	C=O stretch [1, 2, 3]
1608	C=C stretch [1, 3]
1562 and 1501	Ring vibration [1, 3]
1452	Asymmetric CH_2 bend [1]
1350 to 1380	-CH_2 stretch [1]
1148	C-O-C stretch [3]
1014	C-OH stretch [3]
779	2,5-substitution furan ring [1, 2]

Table S4. Atomic percent found using XPS for cleaned Cu, -560 and -700 mV RHE FF ECH fouled Cu electrodes, and pFA on Cu foil.

	C	O	Cu	N	S	Cl
Clean Cu	74.6%	9.76%	13.4%	0.27%	0.00%	1.94%
-560 mV RHE Fouled	68.8%	30.7%	0.00%	0.49%	0.00%	0.00%
-700 mV RHE Fouled	71.4%	28.6%	0.00%	0.00%	0.00%	0.00%
pFA on Cu	81.3%	18.7%	0.00%	0.00%	0.00%	0.00%

Table S5. Reaction data for FA ECH at -560 mV RHE. The humins (model) column is the predicted loss of FA due to homogeneous side reactions predicted by kinetics developed in [4].

	t	**X**	**MB**	**S MF**	**FE MF**	**Humins (Model)**
	min					
ECH1	0	0.000	1.000	0.000	0.000	0.000
	180	0.435	0.616	<0.0024	<0.0014	0.394
ECH2	0	0.000	1.000	0.000	0.000	0.000
	180	0.407	0.593	<0.0023	<0.0011	0.394
ECH3	0	0.000	1.000	0.000	0.000	0.000
	180	0.383	0.565	<0.0023	<0.0007	0.394

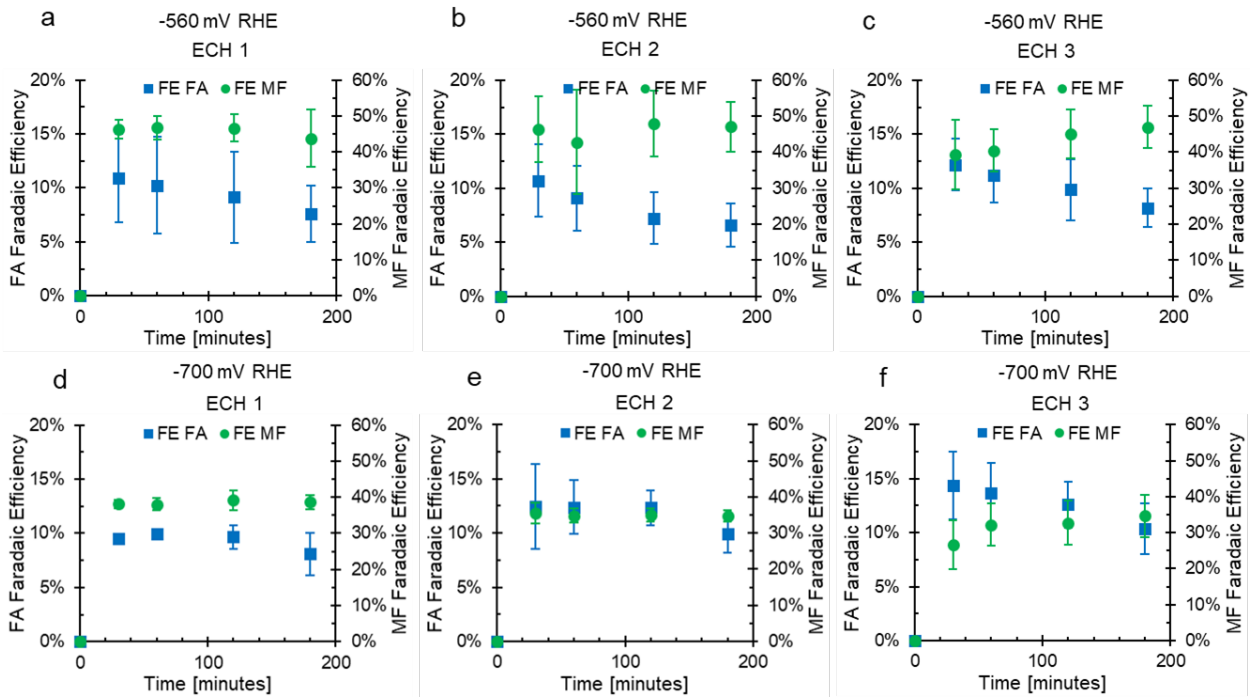

Figure S1. Faradaic efficiency to FA and MF from consecutive ECH of FF with recycled Cu foil electrode. At -560 mV: (a) ECH1, (b) ECH2, (c) ECH3. At -700 mV RHE: (d) ECH1, (e) ECH2, (f) ECH3. Conditions: 200 mM FF, 0.5 M H_2SO_4, 80:20 vol% water:acetonitrile, 3 hour duration ECH, 60 mL N_2 sparging, Cu electrode.

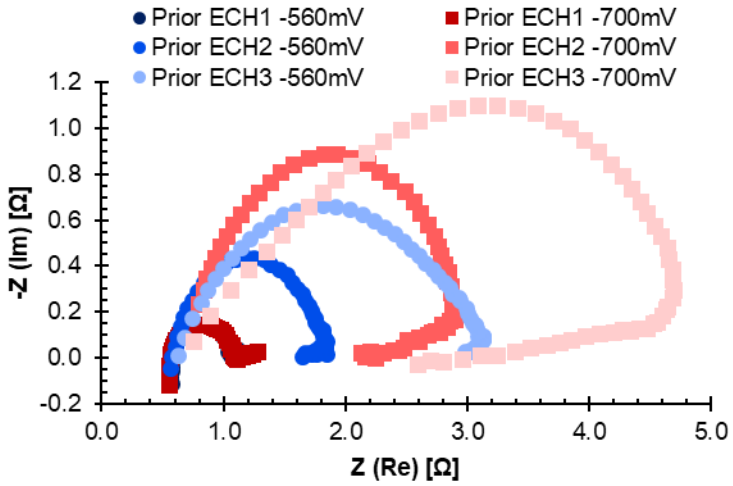

Figure S2. Representative EIS samples prior to ECH. EIS conditions: -560 mV RMS vs RHE, 10 mV AC potential, 100 kHz to 0.1Hz.

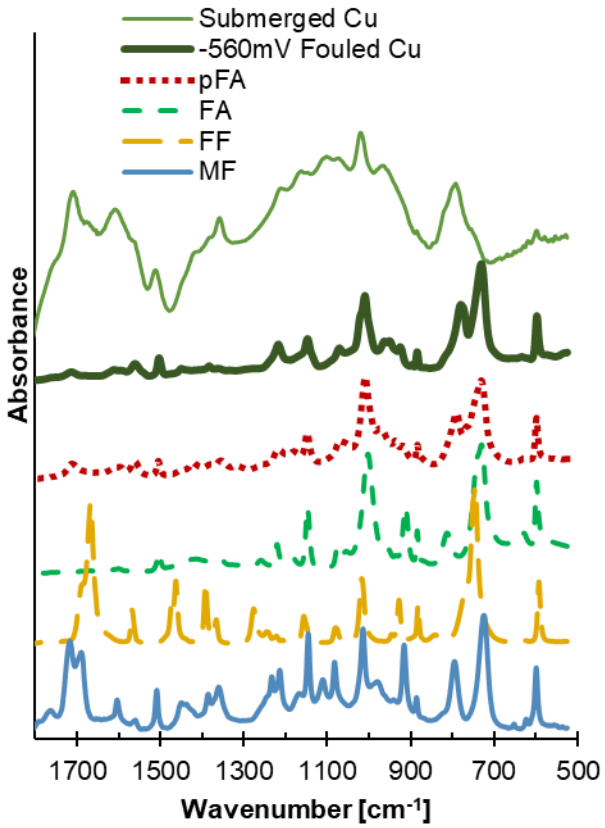

Figure S3. FTIR spectra of Cu submerged in electrolyte (100 mM FF, 30 mM FA) for 3hr (magnified 20x), -560 mV fouled Cu, commercial pFA, FF (magnified 0.6x), FA, and MF (magnified 6x).

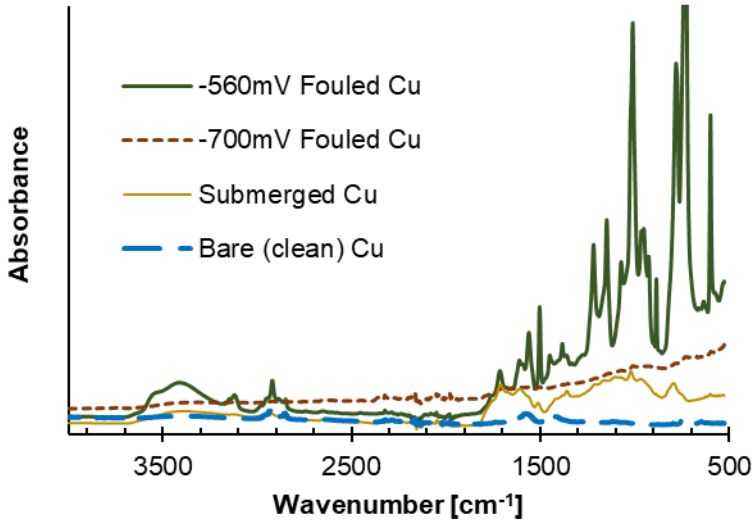

Figure S4. FTIR spectra of -700 mV fouled Cu, -560 mV fouled Cu, Cu submerged in electrolyte (100 mM FF, 30 mM FA) for 3hr, and a bare cleaned Cu foil.

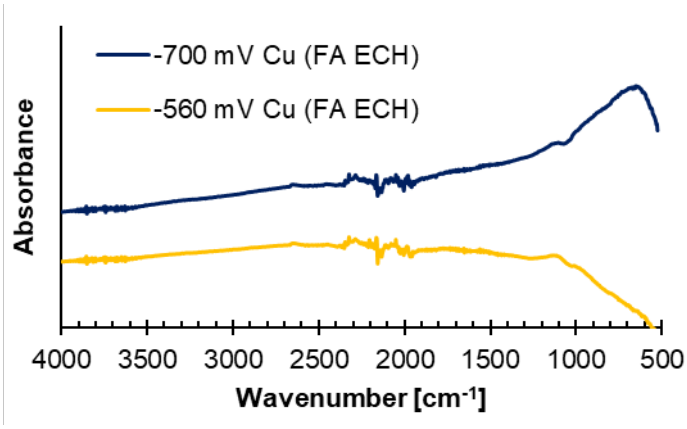

Figure S5. FTIR spectra Cu foil used for FA ECH at -700 mV and -560 mV RHE.

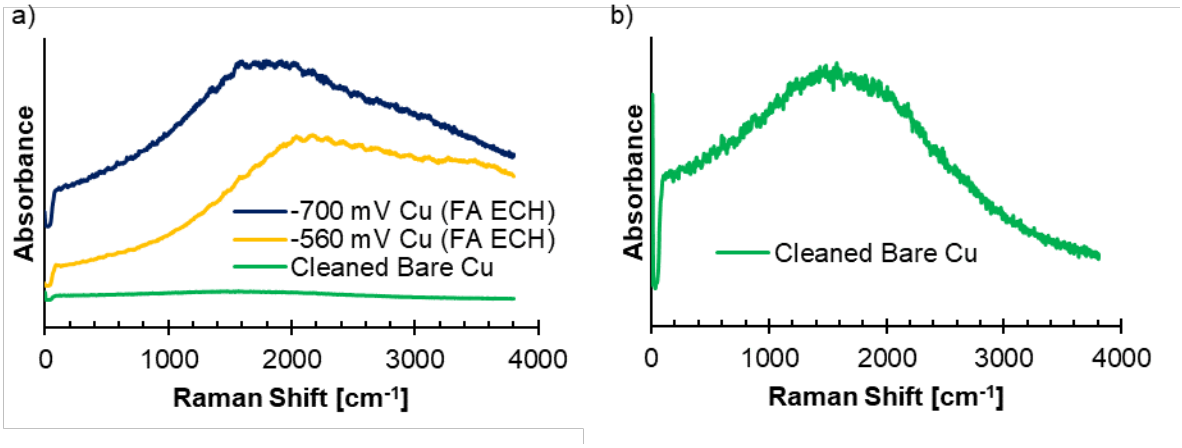

Figure S6. Raman spectra of (a) bare cleaned Cu foil and Cu foil used for FA ECH. (b) magnified scale for cleaned bare Cu foil.

References:

1. Burket CL, Rajagopalan R, Marencic AP, Dronvajjala K, Foley HC. Genesis of porosity in polyfurfuryl alcohol derived nanoporous carbon. Carbon. 2006;44(14):2957-63.
2. Choura M, Belgacem NM, Gandini A. Acid-catalyzed polycondensation of furfuryl alcohol: mechanisms of chromophore formation and cross-linking. Macromolecules. 1996;29(11):3839-50.
3. Nanni G, Heredia-Guerrero JA, Paul UC, Dante S, Caputo G, Canale C, Athanassiou A, Fragouli D, Bayer IS. Poly(furfuryl alcohol)-polycaprolactone blends. Polymers. 2019;11(6).
4. May AS, Biddinger EJ. Modeling competing kinetics between electrochemical reduction of furfural on copper and homogeneous side reactions in acid. Energy Fuels. 2022;36(18):11001-11.