Supporting Information for: Mechanism of p-Substituted Phenol Oxidation at a Ti_4O_7 Reactive Electrochemical Membrane

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1) REM Experimental Setup

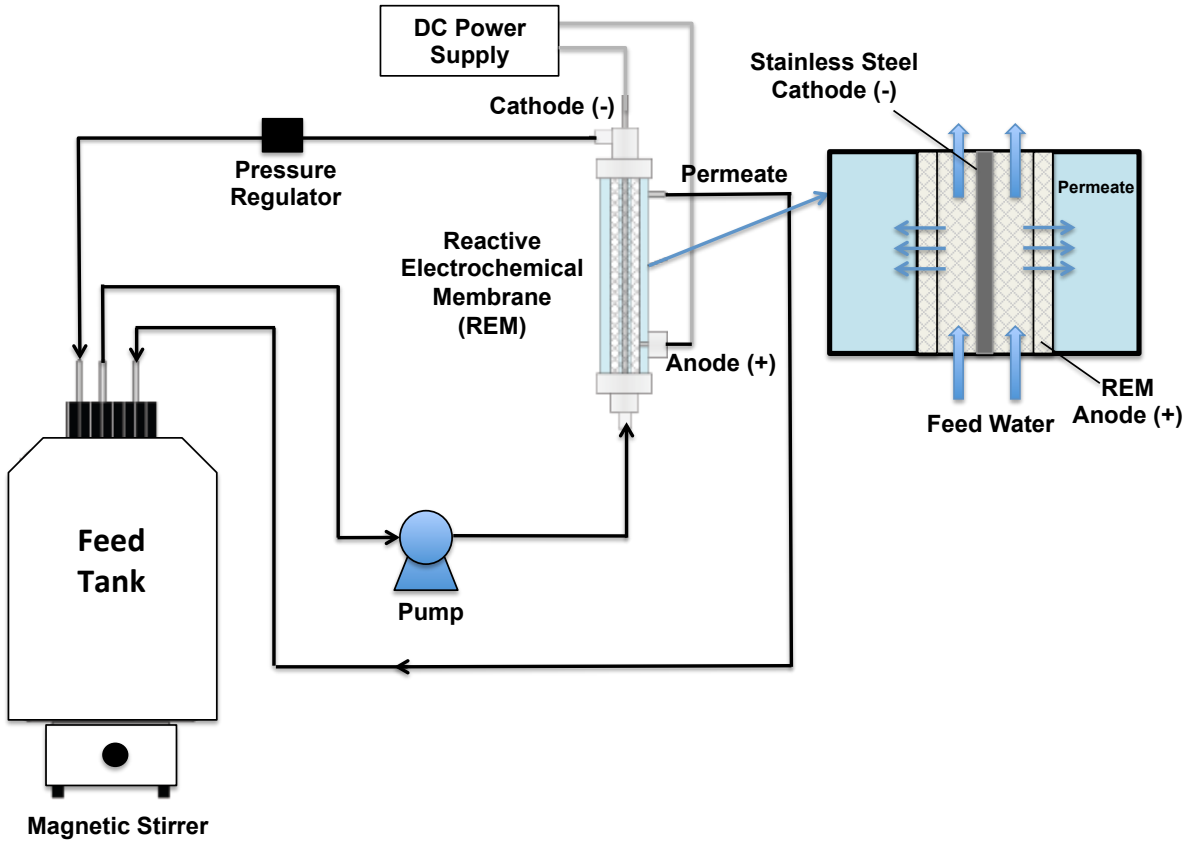

Figure S-1. Schematic of reactive electrochemical (REM) experimental cross-flow setup. Schematic shows setup in 100% recycle mode.

The cross-flow filtration unit is shown in Figure S-1 and contains an Ebonex® REM as anode and 3.18 mm diameter 316 stainless steel rod as cathode. The electrodes were 9.8 mm apart, and their concentric placement creates an isopotential surface on the inner surface of the REM. Solution was pumped through the center of the REM at a constant flow rate (Q = 36 L hr^{-1}). A constant back-pressure of 10 psi was achieved using an adjustable check valve, which forced flow through the REM pores. During cross-flow filtration experiments a constant current density (0—3.5 mA cm^{-2}) was applied to the REM cell using a direct current (DC) power supply (Proteck P6035, Tempe, AZ). Potentials were measured versus a Ag/AgCl reference electrode (Warner Instruments LLC, Hamden, CT) using a Gamry

Reference 600 potentiostat/galvanostat (Warminster, PA). The reference electrode was located 1 mm from the REM surface, and therefore potentials were not corrected for ohmic drop in solution, as it was determined to be negligible. All potentials in this study were reported versus the standard hydrogen electrode (SHE).

2) Experimental Data.

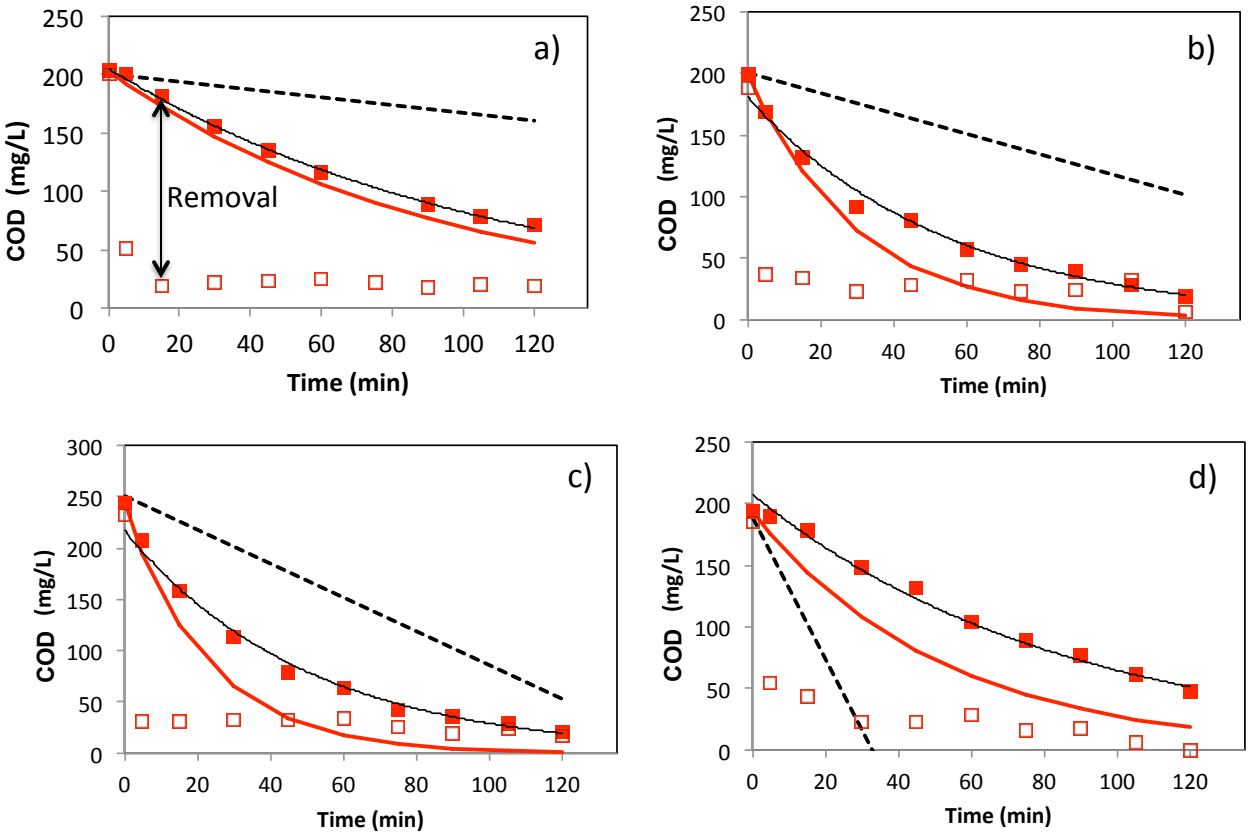

Figure S-2. Profiles of COD concentration versus time where solid squares represent the feed concentration and hollow squares represent the permeate concentration for p-NP oxidation experiments at current densities of: a) 0.2 mA cm^{-2}, b) 0.5 mA cm^{-2}, c) 1.0 mA cm^{-2}, and d) 3.5 mA cm^{-2}. The dashed lines represent current controlled removal at 100% Faradic current efficiency determined by eqn. S-1. The solid red lines represent the mass-transfer controlled rate determined by eqn. S-2. Solid lines through feed data represent a regression line.

$$COD(t) = COD_o - \frac{8At}{FV} \qquad \text{(S-1)}$$

$$COD(t) = COD_o * exp\left[\frac{-k_m At}{V}\right] \qquad \text{(S-2)}$$

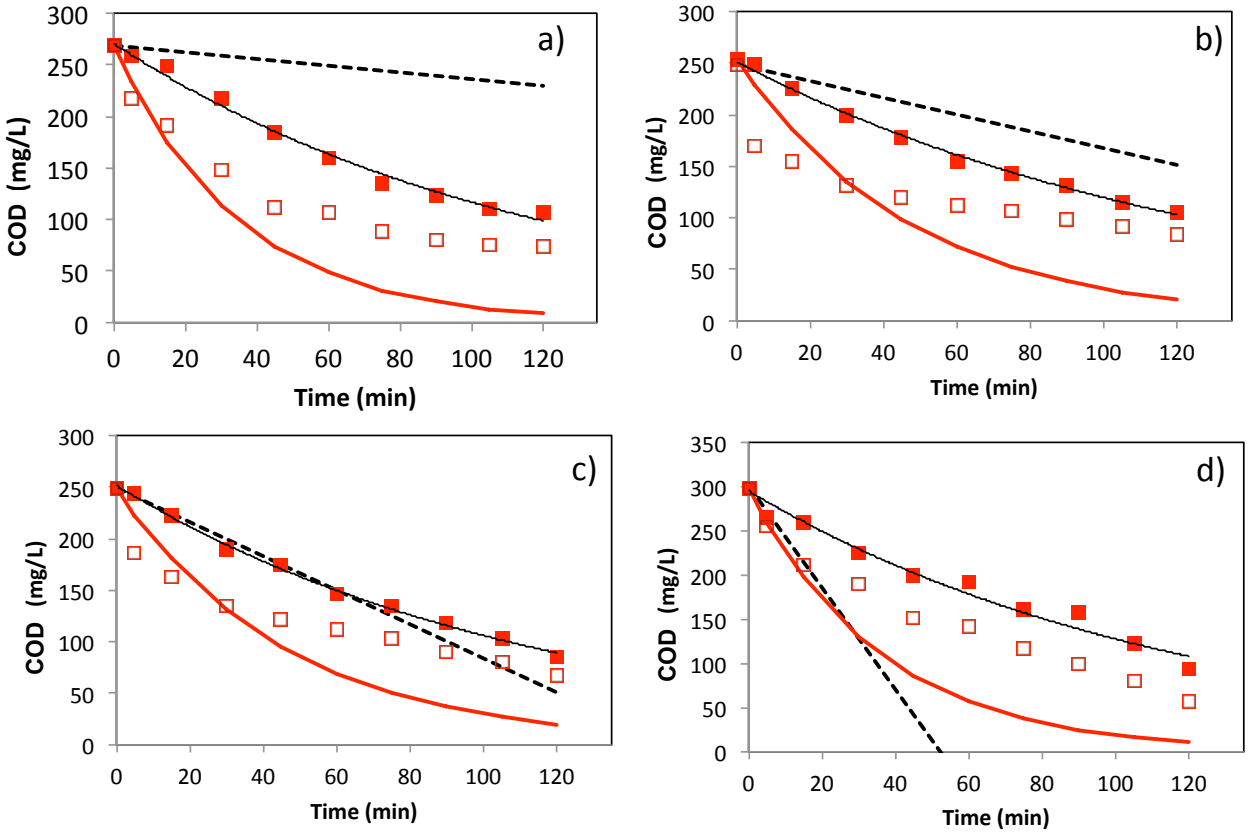

Figure S-3. Profiles of COD concentration versus time where solid squares represent the feed concentration and hollow squares represent the permeate concentration for p-MP oxidation experiments at current densities of: a) 0.2 mA cm^{-2}, b) 0.5 mA cm^{-2}, c) 1.0 mA cm^{-2}, and d) 3.5 mA cm^{-2}. The dashed lines represent current controlled removal at 100% Faradic current efficiency determined by eqn. S-1. The solid red lines represent the mass-transfer controlled rate determined by eqn. S-2. Solid lines through feed data represent a regression line.

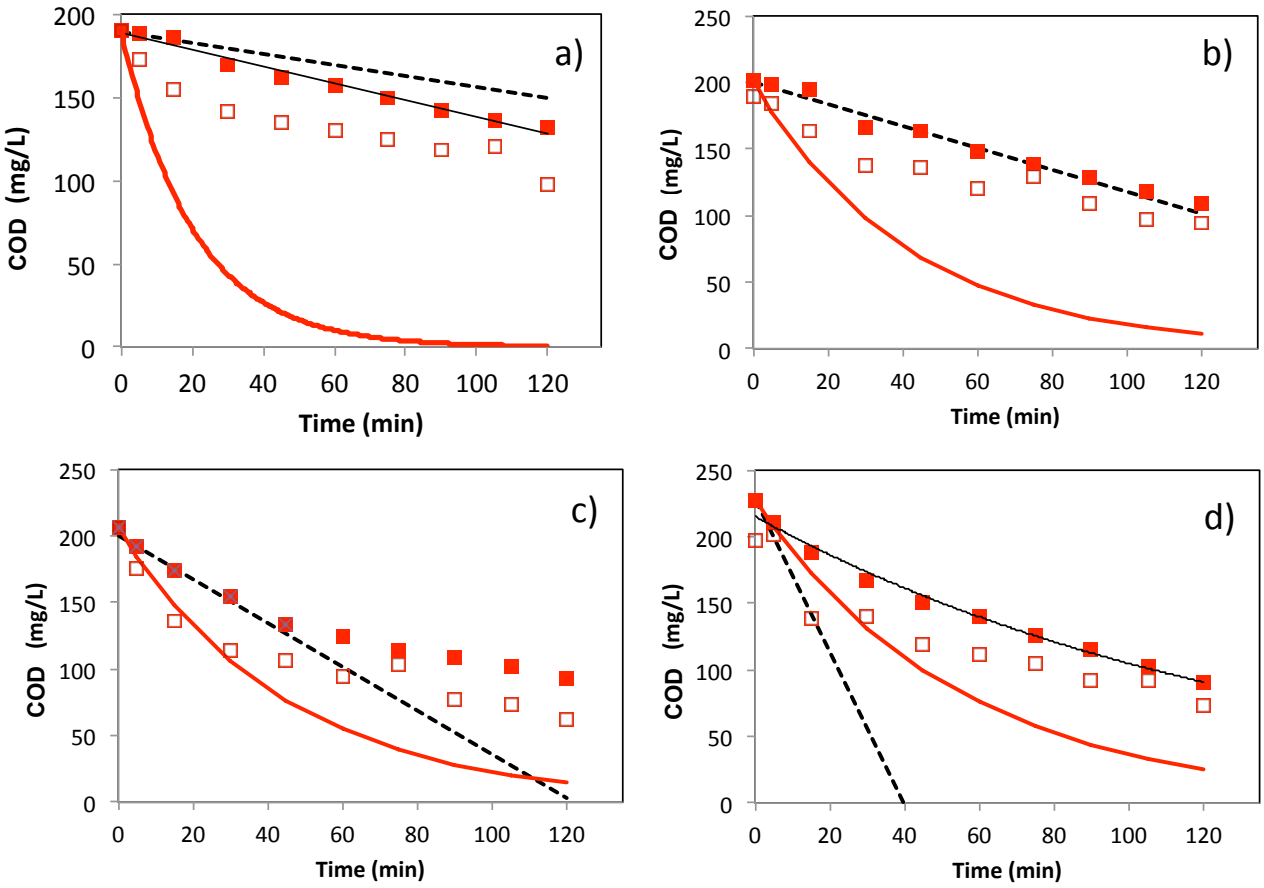

Figure S-4. Profiles of COD concentration versus time where solid squares represent the feed concentration and hollow squares represent the permeate concentration for p-BQ oxidation experiments at current densities of: a) 0.2 mA cm^{-2}, b) 0.5 mA cm^{-2}, c) 1.0 mA cm^{-2}, and d) 3.5 mA cm^{-2}. The dashed lines represent current controlled removal at 100% Faradic current efficiency determined by eqn. S-1. The solid red lines represent the mass-transfer controlled rate determined by eqn. S-2. Solid lines through feed data represent a regression line.

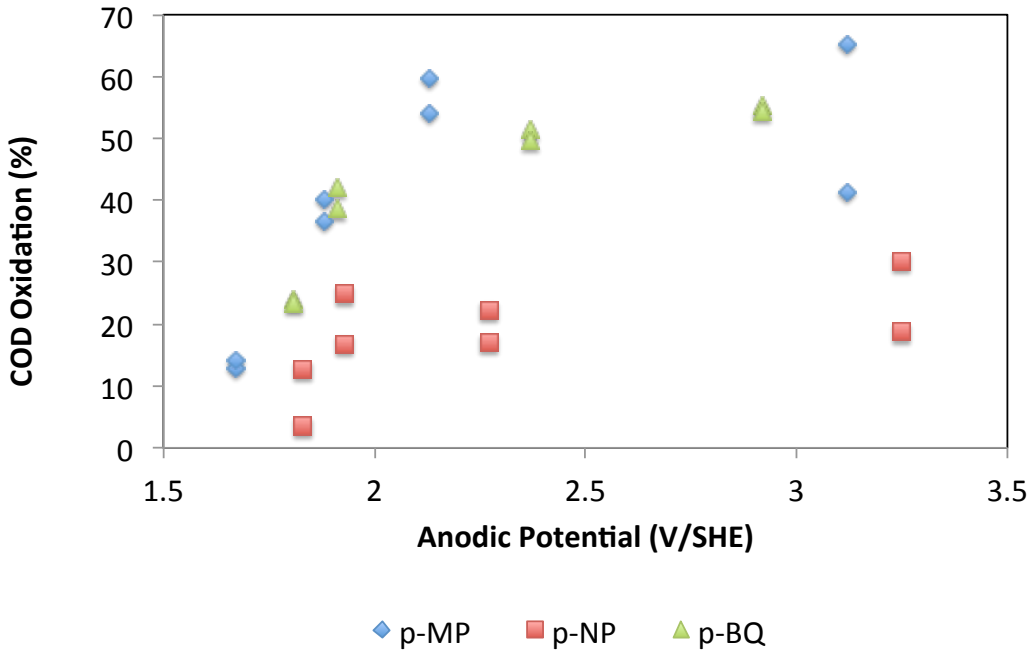

Figure S-5. Percent COD oxidation values from Table 1 versus the measured anodic potential.

3) Fukui Function Values

Table S-1. Listing of Fukui Function values determined by Hirshfeld atomic charges from population analysis data for a) p-MP, p-MP•, and p-MP$^+$ and b) p-NP, p-NP•, and p-NP$^+$.

a)

	p-MP			p-MP•			p-MP$^+$		
Atom	f(elec)	f(nucl)	f(rad)	f(elec)	f(nucl)	f(rad)	f(elec)	f(nucl)	f(rad)
C1	0.128	-0.008	0.06	0.079	0.019	0.049	-0.581	0.068	-0.2565
C2	0.082	0.202	0.142	0.124	0.154	0.139	-0.002	0.132	0.065
C3	0.065	0.178	0.1215	0.031	0.021	0.026	0.093	0.029	0.061
C4	0.125	-0.004	0.0605	0.166	0.156	0.161	0.02	0.18	0.1
C5	0.08	0.209	0.1445	0.027	0.026	0.0265	0.099	0.024	0.0615
C6	0.05	0.186	0.118	0.10	0.124	0.112	-0.004	0.109	0.0525

b)

	p-NP			p-NP•			p-NP$^+$		
Atom	f(elec)	f(nucl)	f(rad)	f(elec)	f(nucl)	f(rad)	f(elec)	f(nucl)	f(rad)
C1	0.1	0.098	0.099	0.048	-0.015	0.0165	0.051	0.037	0.044
C2	0.125	0.016	0.0705	0.16	0.155	0.1575	-0.005	0.165	0.08
C3	0.003	0.087	0.045	-0.005	-0.005	-0.005	0.064	-0.005	0.0295
C4	0.201	-0.005	0.098	0.198	0.169	0.1835	0.049	0.19	0.1195
C5	0.011	0.092	0.0515	-0.005	-0.005	-0.005	0.064	-0.005	0.0295
C6	0.432	0.014	0.223	0.16	0.155	0.1575	-0.005	0.165	0.08