

## Supporting Information for Electrochemical Modulation of Strong Vibration-Cavity Coupling

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1. Bulk and thin cell cyclic voltammograms
2. Example spectra and fits
3. Example fitting to BQ reduction transient
4. Integration of electrochemical charge passed for Faradaic efficiency calculations
5. Table of parameters summarizing electrochemical cycling response of BQ / dHQ

Cyclic voltammograms of BQ : ferrocene (FC) : D<sub>2</sub>O : DMSO in a beaker (Fig. S1a) and thin fluid cell (Fig. S1b). In the bulk cell, the features are clear, classically-shaped CV peaks typically obtained for planar electrodes in bulk solutions. In the thin cell, the cyclic voltammograms obtained for BQ and ferrocene are highly distorted in shape, but give us reasonable estimates of where the various redox processes occur.

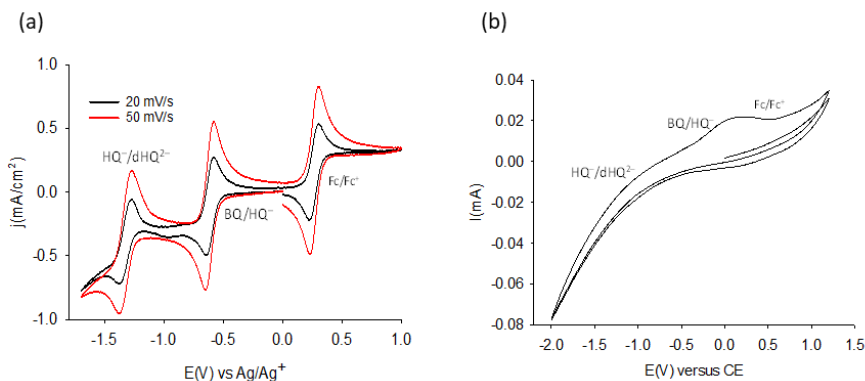


Figure S1.

We highlight that electrochemical kinetics are described by the Tafel equation:

$$i = nFkC \exp[-\alpha(F/RT)(E-E^0)]$$

Where  $n$  is the number of electrons transferred in the reaction,  $k$  is the electrochemical rate constant,  $C$  is the concentration of the electroactive species,  $F$  is Farady's constant,  $E$  is the electrochemical potential applied to the electrode, and  $E^0$  is the formal redox potential of the electrochemical reaction.

If the applied electrochemical potential  $E$  can be reproducibly controlled between experiments, plots of the logarithm of  $I$  versus  $(E-E^0)$  will yield the rate constant  $k$  multiplied by the other terms in the equation.

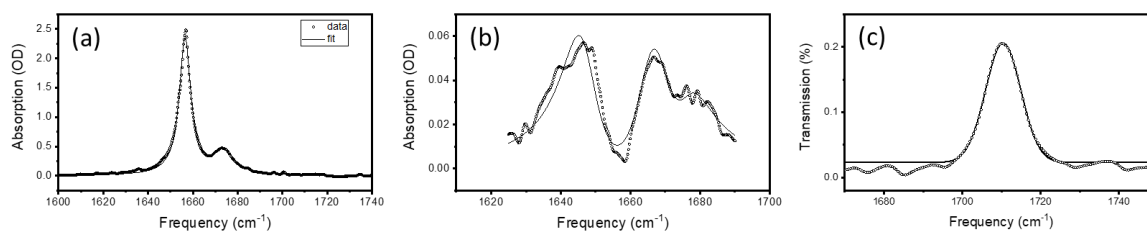


Figure S2.

The example spectrum shown in **Fig. S2a** shows control infrared absorption of 0.3 M BQ in a 50  $\mu\text{m}$  pathlength transmissive cell. From this control spectrum, the extinction coefficients and linewidths of the primary carbonyl peak can be extracted. This spectrum is fit to two Lorentzians yielding peak positions and widths of 1656 and 9  $\text{cm}^{-1}$  for the dominant peak and 1674 and 10  $\text{cm}^{-1}$  for the weaker feature. The weaker peak has an extinction coefficient that is 0.252 x the stronger peak. These values are used when extracting BQ concentration from fits to spectra of coupled systems (**Fig. S2b**). For this extraction, each spectrum is fit using a transfer matrix formalism which treats the BQ absorption as a pair of oscillators with characteristics taken from the control spectrum shown in **Fig. S2a**. We point out here that we have treated our system as a single layer (the BQ solution) bounded by lossless mirrors with a defined reflectivity. This simplification ignores field penetration into the mirror material resulting in an error of cavity length of  $\sim 10$ 's nm (a negligible fraction of the  $\sim 10,000$ 's nm cavity length). This simplification also ignores absorption in the mirror material so our fit does not accurately predict the transmission magnitude, which we account for by using a scaling factor before transmission function. Nonetheless, polariton positions and oscillator concentrations are extracted correctly. Lastly, **Fig. S2c** shows an uncoupled cavity fringe. From a fit to this peak, we extract a cavity linewidth of 9  $\text{cm}^{-1}$ . In all cases, the data are shown as open circles and the fits in solid black curves.

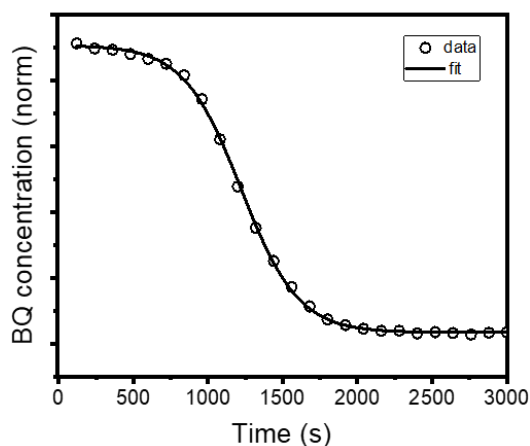
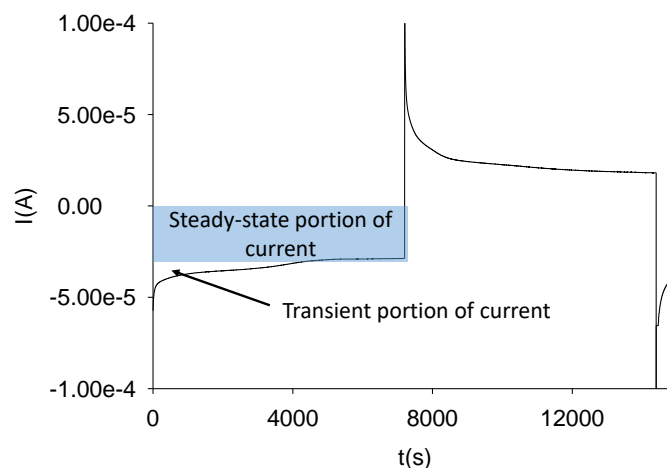
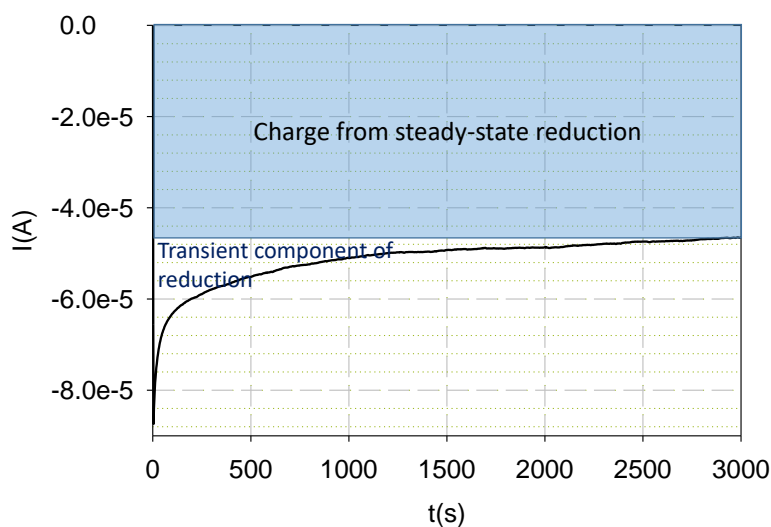


Figure S3.

**Figure S3** shows an example BQ concentration time-series (this is the 25 mm cell data from **Fig. 5a** in the main text) along with the Boltzmann sigmoidal fit that yields a characteristic time constant for this data of 192 s.



**Figure S4** shows how charge was integrated from the spectroelectrochemical time series acquired while system was reduced from BQ to dHQ, as represented in **Fig. 4c** in the main text. Both a long-time (100's to 1000's of seconds) transient and approximately steady-state component of the current are observed.



**Figure S5** shows how charge was integrated from the spectroelectrochemical time series acquired while system was reduced from BQ to dHQ, as represented in **Fig. 5** in the main text (25  $\mu\text{m}$ -thick cell). Both a long-time (100's to 1000's of seconds) transient and approximately steady-state component of the current are observed.

**Table S1.** Comparison of electrochemical conversion of BQ to dHQ as measured spectroscopically and electrochemically (data represented in **Fig. 5**, in the main text—the “half-cavity” cell) for three spacer thicknesses using Faraday's constant ( $Q = 96,484.6$  Coulombs/mole of electrons), assuming full reduction

of the 0.3 M concentration of BQ, and calculating cell volumes by estimating spacer dimensions of ~2.4 cm x 1.4 cm and multiplying by thickness of the spacers in cm. Note that the Faradaic efficiency calculated similarly for the spectroelectrochemical time series data in **Fig. 4** in the main text produced a similar apparent Faradaic efficiency of ~4.

Cavity thickness ( $\mu\text{m}$ )	Benzoquinone (BQ) in cavity (moles/ $10^{-6}$ )	Time to full conversion to dihydroquinone (dHQ) as measured spectroscopically (ks)	Charge passed upon full conversion (spectroscopic) to dihydroquinone dHQ (C)	Apparent electrochemical consumption of BQ (moles/ $10^{-6}$ )	Apparent faradaic efficiency (spectroscopic BQ consumed/apparent electrochemical BQ consumed)
12	1.2	1.5	0.066	0.5	2.4
25	2.5	2.7	0.13	0.7	3.6
50	5	3.5	0.24	1.3	3.8