Supporting Information: Convectional Mass Transport at AC Heated Disk Microelectrodes

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The Supporting Information contains the following material:

Temperature dependence of the standard potential of ferri-ferrocyanide redox systems for different concentrations of KCl (2 M to 0.05 M), electrical connections used in measurements with an ac heated thermocouple microelectrode, a discussion of problems arising from inductance and capacitance in high frequency measurements with microelectrodes (including 4 Figures) and videos showing dielectrophoretc effect (Video S-1), convectional mass transport (Video S-1 and S-2) and jet boiling (Video S-3) on ac heated microelectrodes.

Table S-1. Temperature dependence of the standard potential of the $Fe(CN)_6^{4-}$ / $Fe(CN)_6^{3-}$ redox couple

Solution Composition	ΔE°/ΔT [mV/K]	Standard deviation [mV/K]	R^2 (data points)
50 mM $K_3Fe(CN)_6$, 50 mM $K_4Fe(CN)_6$, 2 M KCl	–1.305	0.008	0.9997 (8)
25 mM $K_3Fe(CN)_6$, 25 mM $K_4Fe(CN)_6$, 1 M KCl	–1.355	0.012	0.9994 (8)
12.5 mM $K_3Fe(CN)_6$, 12.5 mM $K_4Fe(CN)_6$, 0.5 M KCl	–1.431	0.008	0.9998 (8)
5 mM $K_3Fe(CN)_6$, 5 mM $K_4Fe(CN)_6$, 0.2 M KCl	–1.485	0.004	0.9999 (8)
2.5 mM $K_3Fe(CN)_6$, 2.5 mM $K_4Fe(CN)_6$, 0.1 M KCl	–1.526	0.008	0.9998 (8)
1.25 mM $K_3Fe(CN)_6$, 1.25 mM $K_4Fe(CN)_6$, 0.05 M KCl	–1.559	0.003	0.9999 (8)

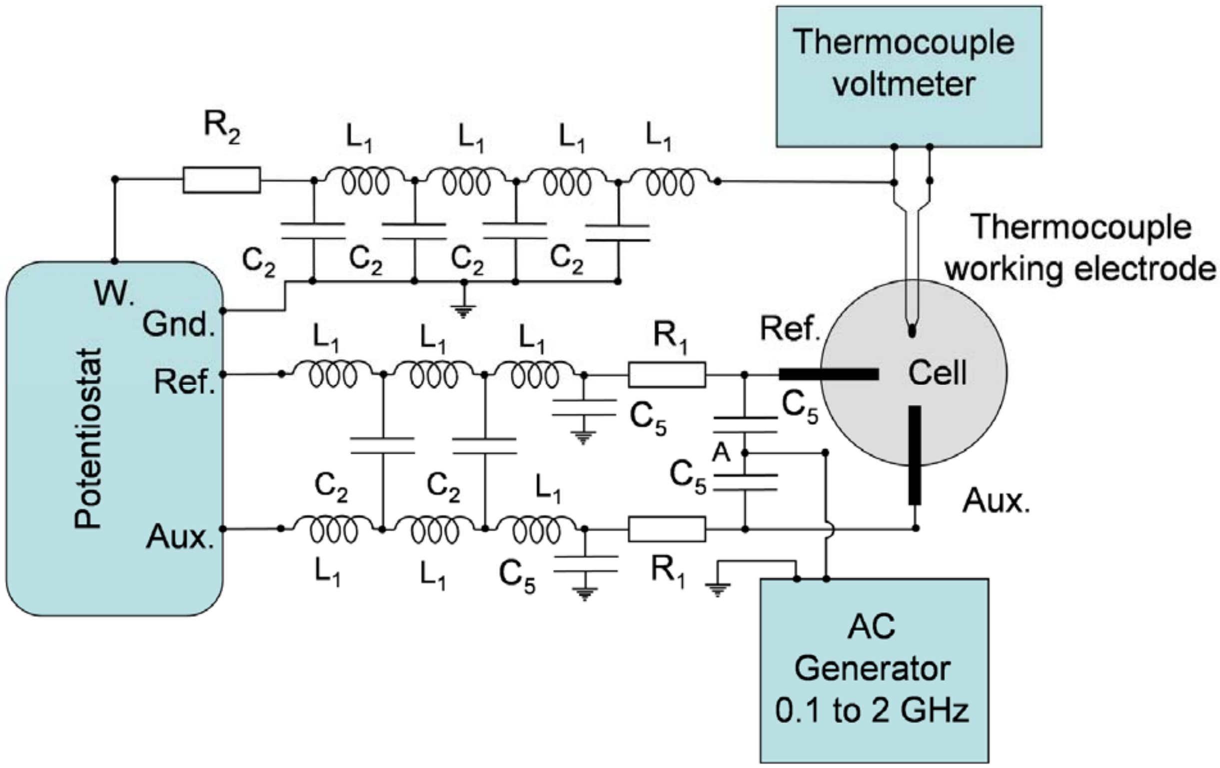


Figure S-1. An interface between a potentiostat, an ac generator and an electrochemical cell used in measurements with a thermocouple microelectrode. C_1 and C_3 are 1 nF capapacitors; C_2, C_4 and C_5 are 10 nF capacitors; R_2 and R_1 are 100 Ω resistors and L_1 is a 33 nH inductor.

The use of high frequency ac modulation in electrochemical systems

In ac heated microelectrodes heat is generated by passing a sufficiently large ac current through the solution resistance; however, this current is also attenuated by the interfacial capacitance of the electrode. In order to minimize this capacitive attenuation (and consequently ac polarization of the electrode interface), the frequency of the excitation signal has to be large (typically larger than 100 MHz). Unfortunately, passing high frequency signals through wired circuits, which are typically used in electrochemical experiments, creates major problems. Short leads can have a very significant inductance. For example, a typical (nonferromagnetic) wire has an inductance of about 8 nH/cm, so a 3 cm lead exhibits an impedance of 150 Ω at 1 GHz frequency. A very small capacitance of 1 pF at 1 GHz exhibits an impedance of only 160 Ω. Furthermore, impedances of inductors and capacitors have opposite signs; consequently, a small inductor (L) in series with a small capacitor (C), at a certain frequency – called the resonance frequency ($f_{res} = \frac{1}{2\pi\sqrt{LC}}$), provides a low impedance (theoretically, zero impedance) path for ac currents. In order to illustrate the role of these electrical artefacts in ac heating, an experiment was performed with a 25 μm Pt disk electrode in 0.5 M KCl containing 12.5 mM $K_4Fe(CN)_6$ and 5 mM KCN. In this experiment the filter board (shown in main paper, Figure 2) was connected directly to the ac generator (without any coaxial cable) and very short (~ 2 cm long) electrodes were plugged directly to the filter board without using any additional leads.

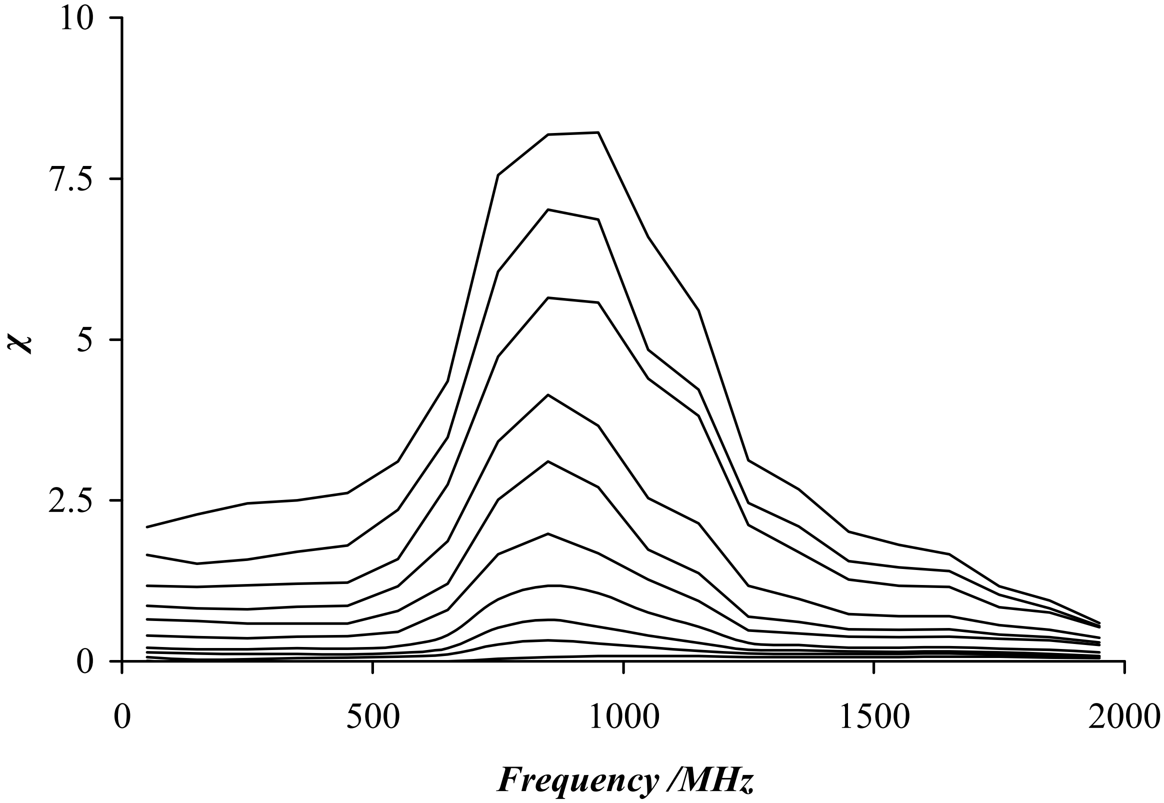


Figure S-2. The limiting current enhancement ($\chi = {i_T}/{i_0} - 1$) plotted as a function of the excitation frequency. Amplitudes of alternating voltage applied to the electrode are shown in Figure S-3. The experiments were performed with a Pt disk electrode (25 μm in diameter) in 0.5 M KCl containing 12.5 mM $K_4Fe(CN)_6$. The dc potential of the working electrode was 500 mV.

With this arrangement it was possible to obtain significant heating of the electrode even at frequencies larger than 1 GHz. The effect of heating can be illustrated by calculating the limiting current enhancement factor ($\chi = {i_T}/{i_0} - 1$, where i_T is the limiting current due to the oxidation of $Fe(CN)_6^{4-}$ measured after applying the ac excitation signal at a given frequency and i_0 is the limiting current without heating). Results obtained for frequencies ranging from 150 to 1950 MHz and for different amplitudes of the excitation signal are shown in Figure S-2. In addition, the magnitude of the alternating potential (ΔV_A) applied to the working electrode at point A (see the insert), was monitored during these measurements and the results are presented in Figure S-3.

The limiting current enhancement factor correlates very well with ΔV_A^4 as it is shown for four different frequencies in Figure S-4.

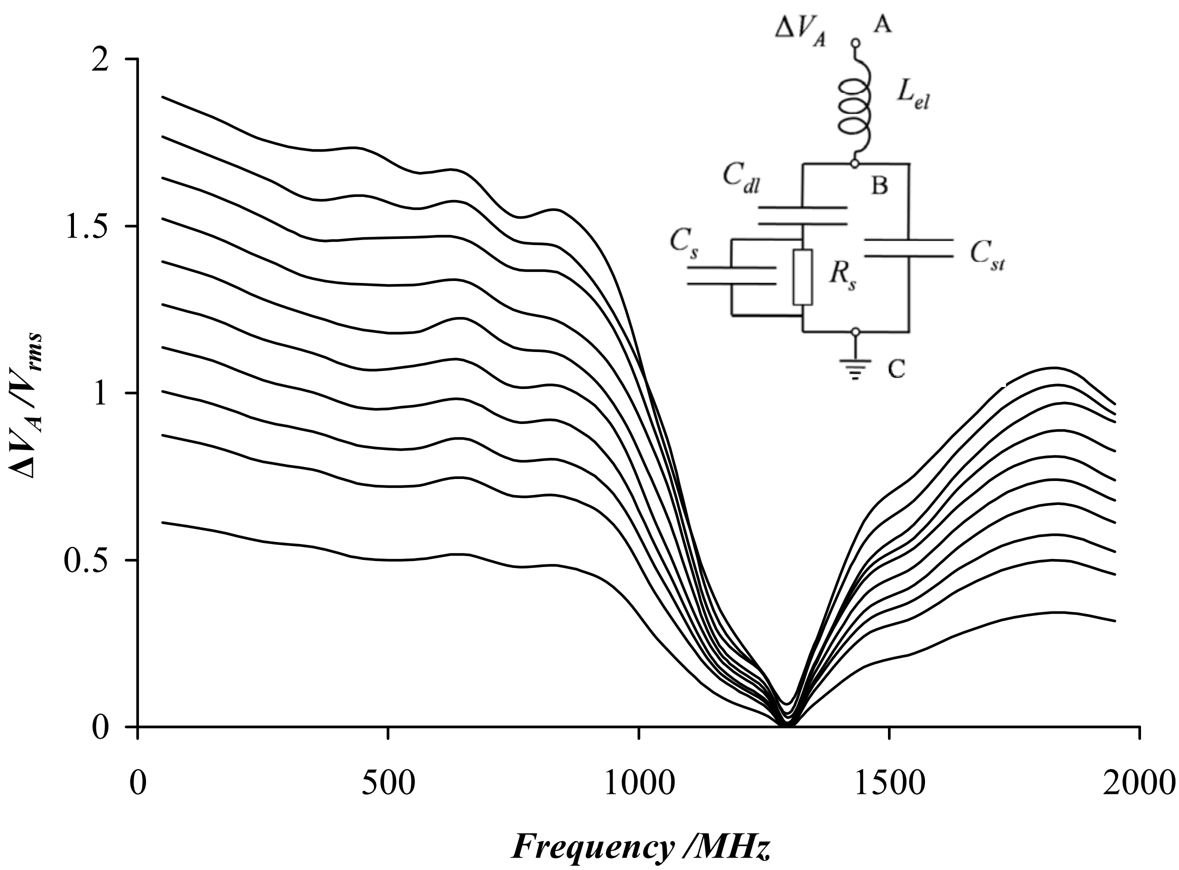


Figure S-3. The magnitude of alternating potential applied to the working electrode lead during the measurements presented in Figure S-2. The insert illustrates a simplified equivalent circuit of the electrode discussed in the text.

The shape of the curves shown in Figures S-2 and S-3 is characteristic of an inductance-capacitance (*LC*) resonance; in this case, the inductance (L_{el}) can be attributed to the short (2 cm) lead of the electrode and the series capacitance arises mainly from the stray capacitance (C_{st}) of the electrode (see the insert in Figure S-3). Other elements in this circuit include the solution resistance, $R_s = \frac{\rho}{4r_0}$ (where ρ is the specific resistance of the solution and r_0 the radius of the electrode) and the solution capacitance, $C_s = 4\varepsilon r_0$ (where ε is the dielectric permittivity of the solution). At this resonance frequency (about 1.3 GHz) the impedance of L_{el} in series with C_{st} drops to almost zero and shunts the 50 Ω output of the ac generator (so in this case the electrode acts as a notch filter). This explains why the ac potential measured at point A drops to almost zero, but the ac current passing through the circuit is still large and the potential difference between points B and C is also quite large. Therefore, at this frequency a substantial current passes through the solution resistance (R_s) and a quite substantial heating of the electrode is observed. In this particular experiment, the maximum heating (which can be attributed to the maximum of power dissipation on R_s) was observed at a frequency of about 850 MHz. It is obvious that the maximum heating frequency depends on the LC resonance, and in practice, is affected by such parameters like the length of the electrode, the thickness of the insulator around the microwire and the depth of immersion of the electrode into the solution.

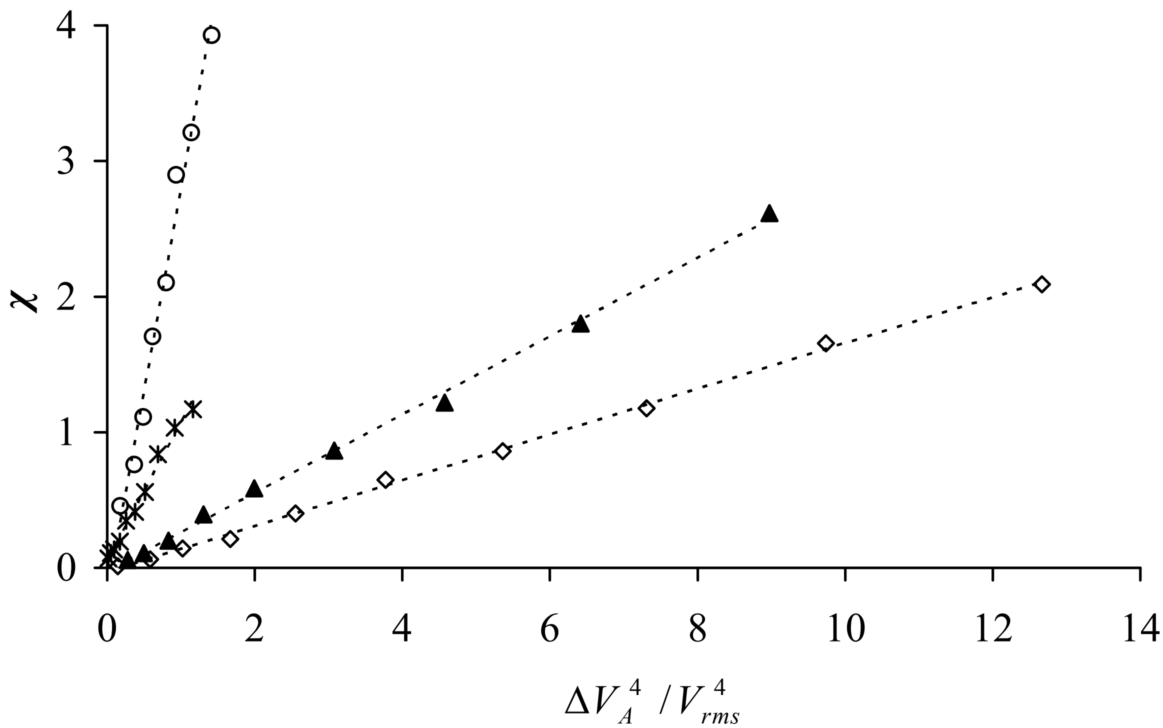


Figure S-4. A correlation between the limiting current enhancement factor and ΔV_{ac}^4 based on data presented in Figures S-2 and S-3. The plots were made for the following frequencies: (◇) 50, (▲) 450, (O) 950 and (∗) 1750 MHz.

The limiting current enhancement factor should depend on the amplitude of potential applied across the solution resistance (ΔV_{Rs}), but we cannot easily tell what ΔV_{Rs} really is, even if we measure the potential (ΔV_A) only 2 cm away from the electrode interface. Some approximate predictions of $\Delta V_{Rs} / \Delta V_A$ are shown in Figure S-5. Values used in these calculations were obtained from properties of the studied system: L_{el} = 16 nH was estimated based on the length of the electrode lead, C_{dl} = 147 pF is the double layer capacitance of the electrode measured at low frequencies, R_s = 3.36 kΩ was calculated from the electrode radius and the specific resistance of 0.5 M KCl, C_s = 0.0347 pF (at 50 MHz) was calculated from the electrode radius and the dielectric properties of water (ε_S = 78.36, ε_∞ = 5.2 and $\tau = 8.27\times10^{-12}$s) and finally C_{st} = 0.913 pF was calculated from L_{el} and the resonance frequency of the system (1.305 MHz). In the same Figure we included a normalized 4th root of $S(\omega) = {d\chi}/{d(\Delta V_A^4)}$ based on experimental data from Figures S-2 and S-3. These two sets of data correlate very well at low frequencies, which may suggest that at least at low frequencies (<1100 MHz) the limiting current enhancement factor is independent of frequency. More detailed discussion of the frequency dependence of the limiting current enhancement factor is provided in the main paper.

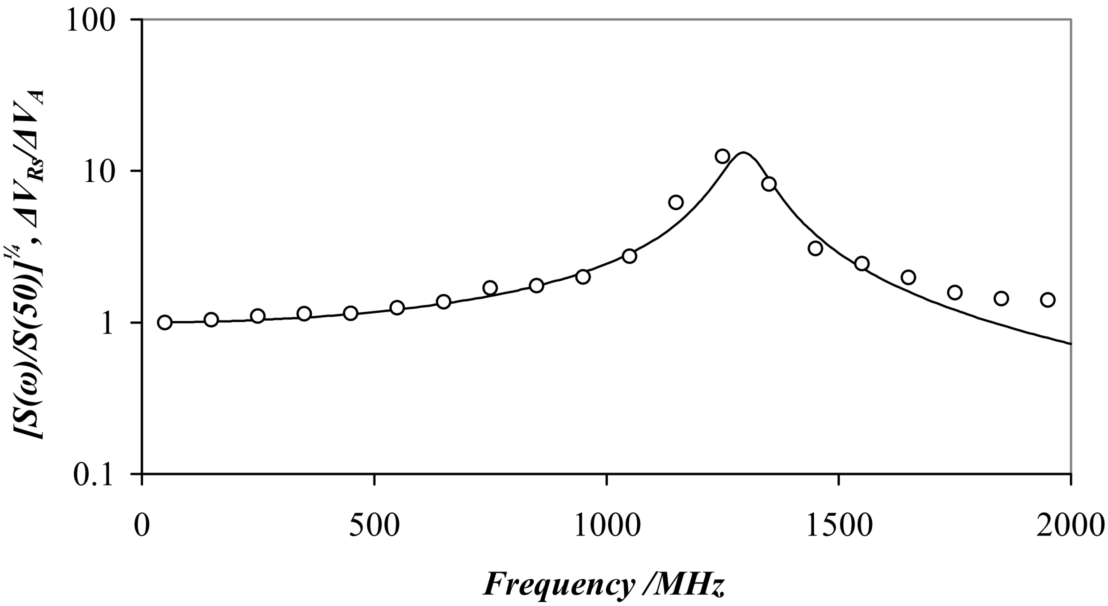
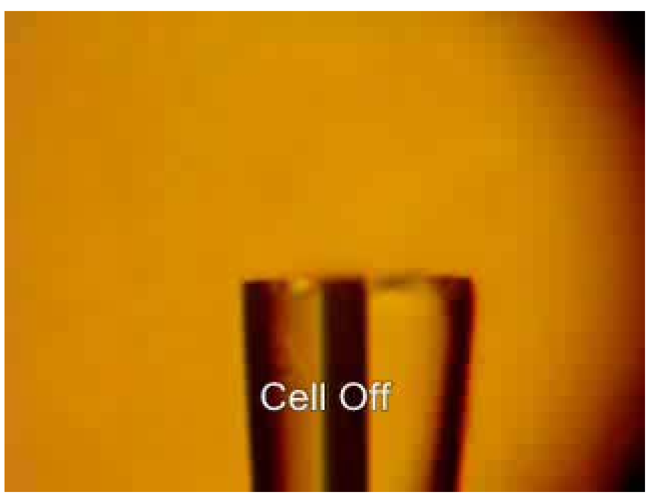


Figure S-5. The ratio of $\frac{\Delta V_{Rs}}{\Delta V_A}$ based on the equivalent circuit from Figure S-3 (with the following values: L_{el} = 16 nH, C_{st} = 0.913 pF, C_{dl} = 147 pF, R_s = 3.36 kΩ, C_s = 0.0347 pF (the frequency dispersion of C_s was taken into account, but this effect is very small).

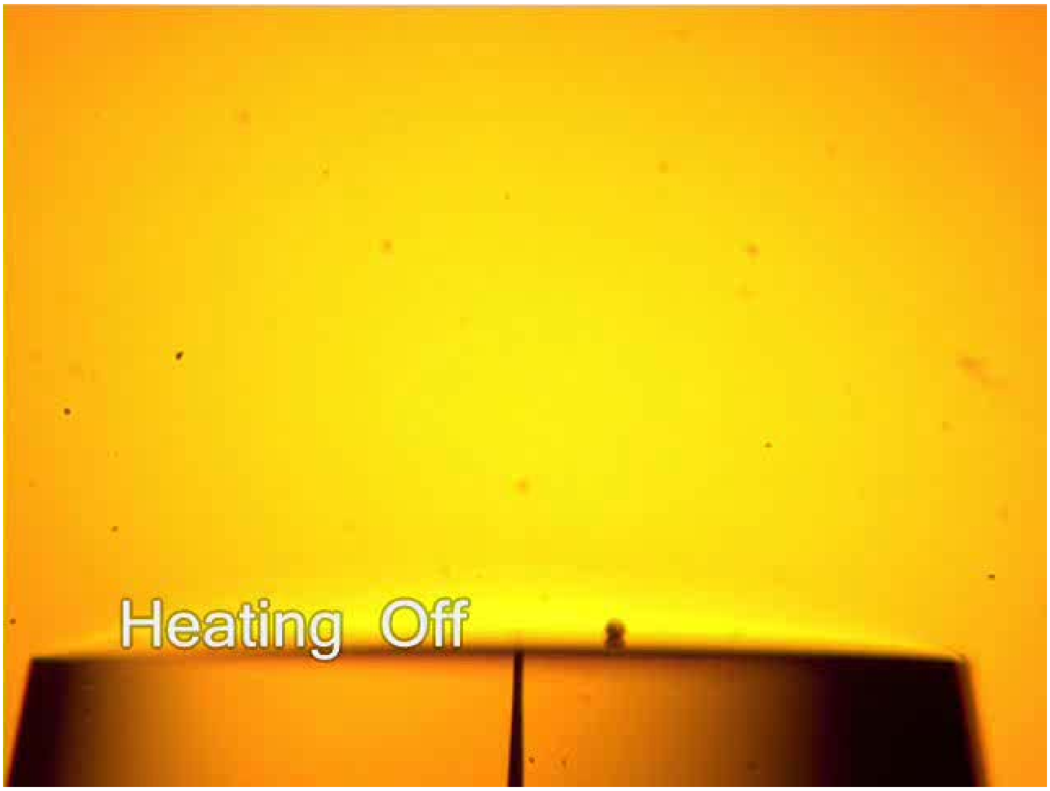
The markers represent a normalized 4th root of $S(\omega) = {d\chi}/{d(\Delta V_A^4)}$ based on experimental data from Figures S-2 and S-3.

Videos below are embedded into the pdf document. They should run under Windows operating system after clicking on the picture. These videos are also provided in a QuickTime format as separate files.

Video S-1. Microscopic observations of convection at a 25 µm Pt disk electrode heated by superposing an alternating voltage of 2.0 V rms at 160 MHz. The solution contained gold microparticles (0.4 to 0.8 µm in diameter) suspended in 0.6 M H_2SO_4. Note a build-up of gold microparticles at the circumference of the electrode.



Video S-2. Effect of heating on the diffusion layer formed during the reduction of 50 mM methyl viologen in 0.5 M NaCl at a 25 µm Pt electrode. The electrode was heated with an alternating voltage of 2.8 V rms at 160 MHz; the dc potential of the working electrode was – 0.5 V vs. SCE. The electrode axis was perpendicular to the gravitational field.



Video S-3. Jet boiling at an overheated 3.6-µm Pt electrode in 2.0 M KCl containing 50 mM methyl viologen. The electrode was heated with an alternating voltage of 2.8 V rms at 165 MHz; the dc potential of the working electrode was – 0.5 V vs. Ag | AgCl(s) | 2 M KCl. The electrode axis and the direction of the jet was perpendicular to the gravitational field. Convection associated with the jet boiling caused a 200 – 300 times increase in the limiting current of methyl viologen.