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Correspondence

Electrochemistry in the Presence of Convective Flow Generated by Acoustic Streaming from a Focused Ultrasonic Source

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Limiting currents for the reduction of hexacyanoferrate-(III), i_{lim}, in aqueous solutions have been recorded in the presence of convective flow generated by a focused acoustic source with its main axis placed normal to the surface of a circular Au electrode embedded in a coplanar Teflon shroud. The results obtained could be fitted to a formula of the type $-i_{lim} = a(U_z^{ss})^b$, where U_z^{ss} is the axial velocity of the fluid along the center line of the lens evaluated at the focal point using computer simulation routines developed by Kamakura and co-workers (Kamakura, T.; Matsuda, K.; Kumamoto, Y.; Breazeale, M. A. *J. Acoust. Soc. Am.* 1995, *97*, 2740−2746). The fit yielded a value of $b \sim 0.5$ in agreement with that of rotating disk and impinging jet electrodes.

Applications of ultrasonics to the field of electrochemistry have steadily gained popularity over the past decade.[1−4] Much of the work so far reported has involved the use of planar horns as sources of acoustic radiation as a means to enhance or modulate mass transport,[5,6] disrupt formation of passive films,[7,8] or alter mechanisms and rates of electrode processes.[2] Useful correlations have been found, for example, between the electrode-to-source distance and applied power and the magnitude of the limiting current, i_{lim}, for redox reactions involving solution-phase species.[3−5] Although the relationships unveiled from these studies may be regarded as largely of an empirical character, the potential utility of this methodology in the analytical field has been amply demonstrated.[1]

A different, albeit closely related approach, involves the use of focused, instead of planar, ultrasonic sources to induce well-defined laminar, as opposed to turbulent, flow. A striking illustration of this effect is given in Figure 1, which shows an image of a column of liquid emerging from the bulk of water during operation of an immersed focused source. Mass flow induced by sound pressure is generally known as acoustic streaming, a phenomenon that has received attention from both experimental and theoretical viewpoints.[9] Although reference to acoustic streaming effects has indeed been made in the sonoelectrochemical literature,[4,7,8] the behavior of electrodes in the presence of the convective flow produced by a focused source has not yet been evaluated. Most importantly, recent theoretical analyses[9] have made it possible to predict quantitatively both the axial and the radial velocity fields as a function of the distance from the focal point. These advances have opened new prospects for the development of a potentially powerful new tool for achieving hydrodynamic conditions similar to wall jet and impinging jet arrangements without the use of mechanical pumps, which mimic, in some cases, those achieved using more conventional rotating disk electrodes.

This brief report provides preliminary results for the reduction of an aqueous solution of potassium hexacyanoferrate(III) on a circular, planar electrode embedded in an insulating plane placed normal to the acoustic axis of a focused source. Polarization curves obtained in this geometry were of a sigmoidal-type shape yielding, except for extreme conditions, well-defined limiting currents, which varied both with the power of the source and with the distance from the focal point.

EXPERIMENTAL SECTION

Measurements were performed in an all-acrylic cell shown schematically in Figure 2. The working electrode was a gold disk (A, 4-mm radius) of a Au−Au rotating ring-disk assembly (RRDE, Pine Instruments), which was inserted through a Teflon adapter, E, mounted on the smaller, side square section of the cell along the principal axis of the acoustic transducer, D. The distance between the working electrode and the transducer, denoted as

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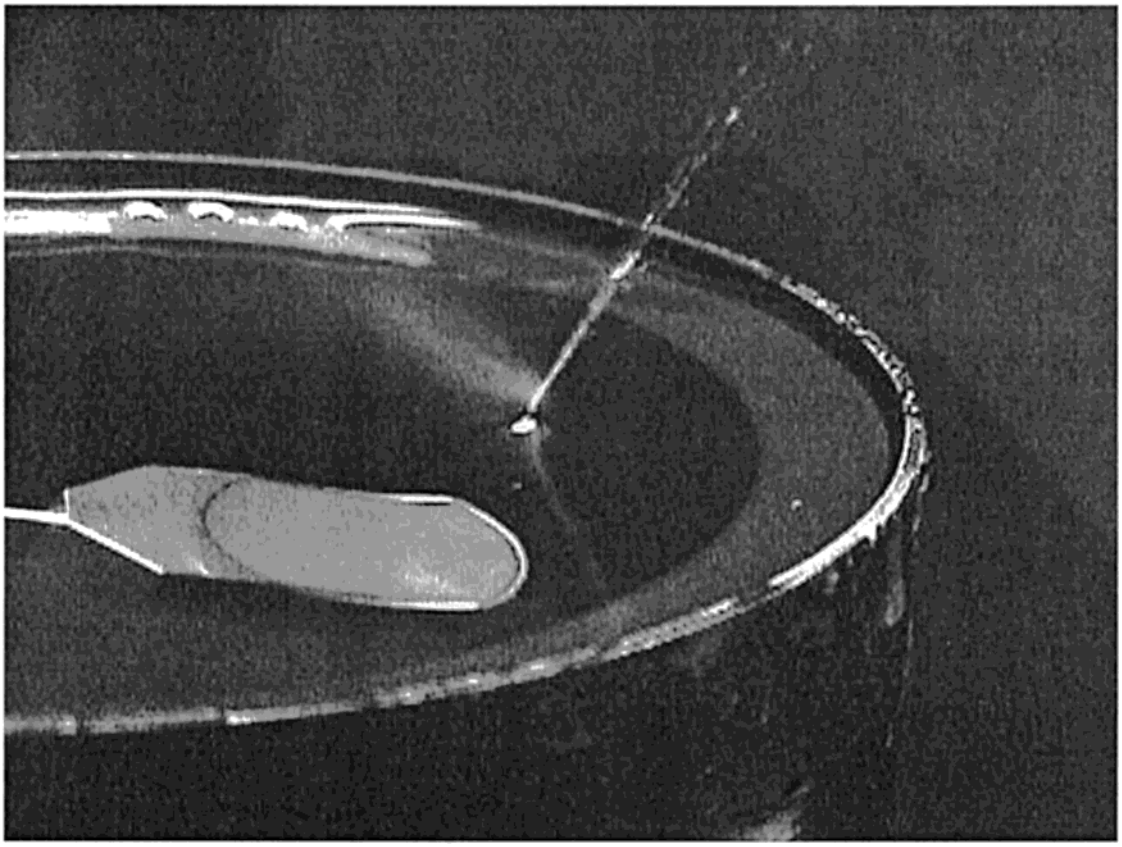

Figure 1. Image of a column of liquid emerging from the surface of water induced by acoustic streaming generated by an immersed focused ultrasonic source.

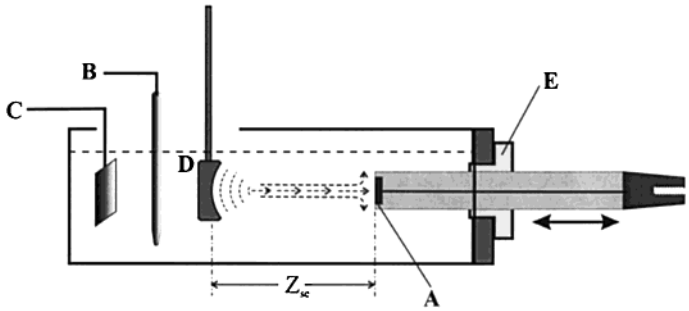

Figure 2. Schematic diagram of the all-acrylic cell for electrochemical measurements in the presence of convective flow generated by a focused acoustic source. A. working electrode; B, reference electrode; C, counter electrode; D, acoustic transducer; and E, Teflon adapter. The arrows represent idealized streamlines.

Z_{se} in Figure 2, could be adjusted by sliding the electrode along E, as indicated in the figure. Accurate control of Z_{se} in the range 35−60 mm away from the transducer was achieved by connecting D to an electrically actuated positioner (not shown in the figure). A saturated calomel electrode (SCE), B, and a gold foil, C, were used as reference and counter electrodes, respectively. Polarization curves were recorded at a scan rate of 50 mV/s in nondeaerated 25 mM $K_3Fe(CN)_6$ (Sigma, 99%) aqueous solutions using a Pine potentiostat and a Yokogawa *XY* recorder. For this concentration of reactant, the lack of supporting electrolyte may elicit an error no larger than ∼6%.[10] The transducer, D, was a piezoelectric device with a nearly circular concave surface (3.1-cm diameter, 4.0-cm radius of curvature, i.e., focal distance). The associated electronics consisted of a function generator (Hewlett-Packard P3314A), which drove a power amplifier (ENI 325LA). The transducer was driven by the amplifier in continuous wave (CW) mode at 4 MHz, its resonant frequency.

RESULTS AND DISCUSSION

A series of cyclic voltammetry curves as a function of source power, P_w, recorded at $Z_{se} = 45$ mm, that is, 5 mm away from the focus, are shown in curves a through k, Figure 3. As indicated, an increase in P_w brings about a gradual change in the shape of the polarization curves from the usual behavior in quiescent media (curve a) to convective diffusion at the higher powers, together with an increase in the values of the limiting currents, i_{lim}, for hexacyanoferrate(III) reduction, consistent with an enhancement in the mass transport rates. Insight into the fluid motion generated by the acoustic source was gained by performing simulations based on the model and associated software developed by

(10) Newman, J. *Ind. Eng. Chem. Fundam.* **1966**, *5*, 525−529.

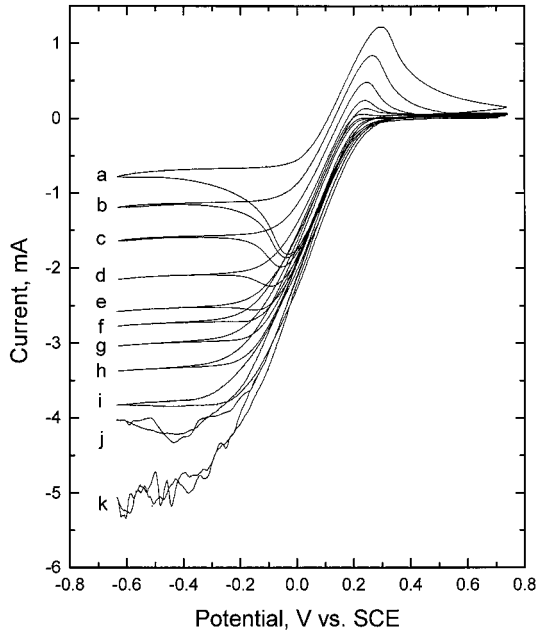

Figure 3. Series of cyclic voltammetry curves for a Au electrode in an aqueous 0.025 M $K_3Fe(CN)_6$ solution recorded at $Z_{se} = 45$ mm as a function of the applied power P_w: a, 0; b, 0.07; c, 0.15; d, 0.32; e, 0.54; f, 0.73; g, 0.94; h, 1.30; i, 2.05; j, 2.95; and k, 4.03 W (see text for details).

Kamakura et al.[9] with the actual experimental parameters as input. This program provides numerical solutions for the continuity equation (eq 1 below) coupled to the time-dependent Navier–Stokes equation for an incompressible fluid in cylindrical coordinates (eqs 2 and 3) subject to the appropriate initial and boundary conditions, namely

$$\frac{\partial U_z}{\partial z} + \frac{1}{r}\frac{\partial}{\partial r}(rU_r) = 0 \tag{1}$$

$$\frac{\partial U_z}{\partial t} + U_r\frac{\partial U_z}{\partial r} + U_z\frac{\partial U_z}{\partial z} = F_z - \frac{1}{\rho_0}\frac{\partial P}{\partial z} + \nu\left[\frac{\partial^2 U_z}{\partial z^2} + \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial U_z}{\partial r}\right)\right] \tag{2}$$

$$\frac{\partial U_r}{\partial t} + U_r\frac{\partial U_r}{\partial r} + U_z\frac{\partial U_r}{\partial z} = F_r - \frac{1}{\rho_0}\frac{\partial P}{\partial r} + \nu\left[\frac{\partial^2 U_r}{\partial z^2} + \frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial r}(rU_r)\right)\right] \tag{3}$$

where P is pressure, U_r and U_z are the components of the velocity vector along the radial, r, and axial, z, directions, respectively; ρ_0 is the density of the fluid under quiescent conditions; and $\nu = \eta/\rho_0$, the kinematic viscosity, where η is the shear viscosity. The terms F_r and F_z in eqs 2 and 3 are the components of the driving force F responsible for fluid streaming. As discussed by Gusev and Rudenko,[11] F, for this problem, is expressed as a sum of various terms; however, under the conditions of these experiments, only one of such terms becomes dominant, namely,

$$F = -\frac{1}{\rho_0^2}\left(\zeta + \frac{4\eta}{3}\right)\overline{(\rho_a \nabla^2 v_a)} \tag{4}$$

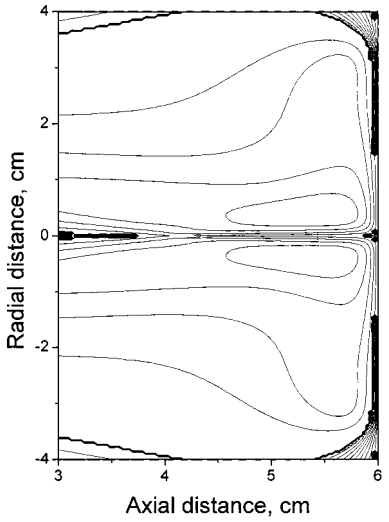

Figure 4. Set of streamlines obtained at a time $t = 5$ s after the acoustic source is turned on, as calculated using a simulation package developed by Kamakura et al.[9]

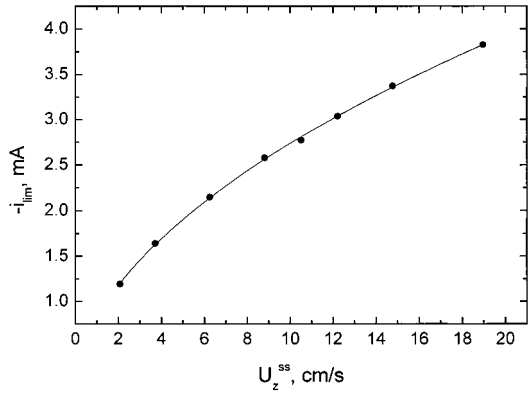

Figure 5. Plot of the limiting currents $i_{lim,}$ in curves b through i in Figure 3, as a function of the axial velocity U_z^{ss} calculated from theory (see text).

where ρ_a is the density perturbation, ζ is the bulk viscosity, and v_a is the particle velocity. Subsequent introduction of both the vorticity, ω, and stream functions, ψ, in terms of U_r and U_z, that is,

$$\omega = \frac{\partial U_r}{\partial z} - \frac{\partial U_z}{\partial r}; \quad U_z = \frac{1}{r}\frac{\partial}{\partial r}(r\psi); \quad U_r = \frac{\partial \psi}{\partial z} \tag{5}$$

reduces the problem to Poisson's equation

$$\frac{\partial^2 \psi}{\partial z^2} + \frac{\partial}{\partial r}\left[\frac{1}{r}\frac{\partial}{\partial r}(r\psi)\right] = -\omega \tag{6}$$

subject again to the appropriate initial and boundary conditions.

As a means of illustration, Figure 4 shows a set of streamlines obtained at a time $t = 5$ s after the acoustic source is turned on, assuming the wall is at 6 cm away from the transducer. As indicated therein, the fluid downstream from the focal point at 4 cm is characterized by a tightly defined region of high density of streamlines that is consistent with a high velocity gradient, as

(11) Gusev, V. E.; Rudenko, O. V. *Sov. Phys. Acoust.* **1979**, *25*, 493–497.

expected for a jet, surrounded by a region of low density of streamlines or, equivalently, relatively stagnant media.

Inspection of the temporal behavior of the streamlines made it possible to determine the time at which local steady-state conditions were achieved within the region of relevance to the electrochemical experiments, which was found to be of the order of a few seconds. Implicit in this model is the fact that the electrode is assumed to be embedded in the cell wall opposite to the transducer.

Correlations between i_{lim} and the axial velocity at the focal point of the source denoted as U_z^{ss} were sought via the expression, $-i_{lim} = a(U_z^{ss})^b$ using values of U_z^{ss} determined theoretically as specified above (see scattered points in Figure 5) for the actual conditions selected for these experiments. Excellent agreement was obtained for $a = 9.142$ and $b = 0.523$ (see line in this plot). Although the preexponential factor a may be regarded at this point as purely phenomenological, the exponent $b \sim 0.5$ is in precise agreement with that found for the rotating disk or jet impinging electrodes in the wall tube regime,[12] providing rather unambiguous evidence that the hydrodynamic conditions for all of these systems are, indeed, equivalent.

On the basis of the preliminary results presented in this work and more detailed experimental and theoretical studies now in progress in our laboratories, acoustic streaming using a focused source may be expected to provide unparalleled advantages compared to more conventional forced-convection systems, such as rotating disk (RDE), and channel- and tube-type electrodes, particularly in situations in which operation of moving devices or pumping of fluids would not be within easily realizable reach. In fact, the range of fluid velocities achieved using the present acoustic source corresponds to rotation rates for an RDE between 300 and 5000 rpm (the last measurement attempted for which the fluid motion did not reach the turbulent regime). Especially attractive are electrochemical studies in constrained geometries and harsh environments, including high pressures, low and high temperatures, and those involving hazardous materials, as well as analyses of small amounts of electroactive materials. Also envisioned is the implementation of acoustically modulated hydrodynamic flow to reproduce conditions obtained with speed modulation of rotating disk electrodes in a fully quantitative fashion.[13]

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