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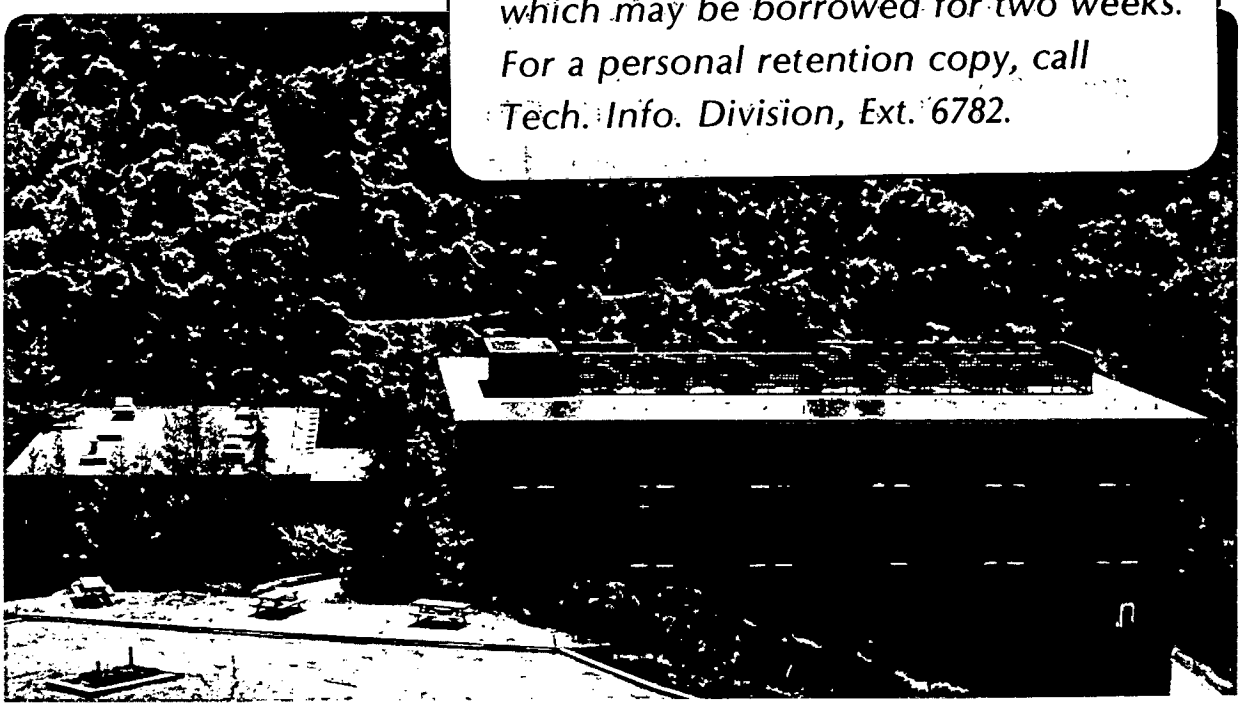

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EFFECT OF SUSPENDED PARTICLES ON THE RATE OF MASS TRANSFER TO A ROTATING DISK ELECTRODE*

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ABSTRACT

The addition of 0-40 vol % spherical glass particles of 4-75 μm diameter to the electrolyte has been found to significantly increase limiting currents for the reduction of $Fe(CN)_5^{-3}$ on rotating disk electrodes. The increase is largest, more than three-fold, at high rotation speeds (2870 rpm), large electrodes (1.41 cm radius), high particle content (40 vol %) and intermediate particle diameter (approx. 10 μm). Calculations of viscous power dissipation have shown that increasing limiting current by the addition of particles at constant rotation rate requires a much lower increase in stirring power than that required for obtaining the same limiting current by use of higher rotation rate in the absence of particles. A tentative theoretical model, involving mass transfer enhancement by means of a fresh fluid layer entrained by rotating particles, provides reasonable agreement with observed behavior.

INTRODUCTION

Inert solid particles of nonconducting materials suspended in moving electrolytes have long been used to enhance mass transfer to electrodes,[1-3] and solids suspended in a liquid rapidly flowing tangentially to a wall have been shown to increase the rate of heat and mass transport to the wall several-fold.[4-6] The mechanism for this enhanced transport is, however, only poorly understood. Dworak and Wendt[7] suggested that for liquid-liquid emulsions, the droplets cause increased turbulence in the outer hydrodynamic boundary layer and have the effect of compressing the mass transfer boundary layer. Turbulence has also been postulated to cause some particles to randomly move towards the wall bringing bulk solution entrained in their own boundary layers[5] or even destroying[8] the boundary layer of the surface by their impact. Ahuja,[4] noticed a direct relationship between increase in heat transfer and velocity gradient and proposed that his polystryrene beads rotated and spun off solution radially. The question therefore arises whether the rotation of particles induced by the local velocity gradient is an important factor and whether the convective disturbance exists throughout the boundary layer or only in the vicinity of the particles.

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This work[9] was undertaken to characterize the increase in mass transfer to a rotating disk electrode caused by suspended spherical glass particles by the measurement of limiting currents for the reduction of ferricyanide.

EXPERIMENTAL

Tapered epoxy disks of overall diameter of 3.83 cm with nickel active surfaces of 1.13 and 2.83 cm diameter were used. Rotation rates ranged from 387-2870 rpm. Particles of soda-lime glass (Potters Industries, Hasbrouck Heights, NJ, density 2.46-2.49 g/cm^3) were added in six narrow size ranges (Table I) at volume fractions of 0 to 40%. Mean diameters, ranging from 4-75 μm were determined by optical and scanning electron microscopy. The rotating disk was submerged in a beaker of 7.3 cm diameter of 6.5 cm height (Fig. 1). It contained a cylindrical nickel counter electrode of 79 cm^2 area, a nickel reference electrode, a magnetic stirrer to keep the particles suspended, baffles and a sealed top to keep particles and solution from escaping at high rotation rates. The electrolyte composition was 1.97 M NaOH, 0.2 M $K_4Fe(CN)_6$.

For every experimental run, the cell was filled with 218 ml of fresh solution. The limiting currents for reduction of ferricyanide were determined at rotation rates of 40.5 to 300.5 radians/s (387 to 2870 rpm), by use of a PAR 371 potentiostat (galvanostatic mode). The rate of current advance was less than 1 mA/s. A given size glass beads was then added to the cell by weight and solution was removed to keep the total volume of the suspension constant. Thus, limiting current measurements were made with both RDEs over the same range of rotation speeds with gradually increasing particle content.

The reproducibility of limiting current measurements was about ± 8% and is illustrated in Fig. 2. Decomposition of the ferrocyanide and limited accuracy in correcting for temperature variations, which amounted up to 12°C, are the primary causes for the scatter in the measurements. In the absence of particles, limiting currents close to those expected on the basis of rotating disk theory were obtained (Fig. 3). The deviation is within the experimental reproducibility and may be explained by the relatively small volume of the cell and the presence of the baffles.

EXPERIMENTAL RESULTS

The experimental results show that limiting current depends on disk diameter, rotation speed, particle diameter and volume fraction. Figures. 4-7 show measured points fitted by cubic spline curves. As particles are added to the solution, the limiting current remains unaffected until a threshold concentration is reached (Fig. 4). Limiting current then increases rapidly and reaches, at the highest volume

fraction, over 3 times its value without solids. The increase is smaller at lower rotation rates. With the smaller disk (Fig. 5) the effect is qualitatively the same, but the increase is smaller (two-fold). The dependence of limiting current on rotation rate changes with increasing particle content from the classical square root function in the absence of particles to an almost linear dependence at high particle content. This trend is more pronounced for the smaller particles (Fig. 6). The effect of particle diameter is illustrated in Fig. 7. The increase in limiting current density is greatest for particles of about 10 μm diameter. The optimum particle size is slightly larger than the mass transfer boundary layer thickness and shifts to smaller values with increasing rotation rate (the cubic spline curves shown in Fig. 7 are affected by adjacent data points that do not lie in the plane of measured data shown).

The multivariant experimental results have been represented by cubic spline functions which can be shown in 3-dimensional plots to summarize the observed results. Figure 8 illustrates how the optimum particle size becomes more pronounced with increasing solids content. Figure 9 shows that the effect of solids content is more significant at higher rotation rates.

THEORETICAL MODELS

Two theoretical models which consider different mechanisms for the transport of fresh solution to the electrode surface by the action of the particles have been investigated. Both of these models assume that the glass spheres are not in contact with the disk electrode but move parallel to it, along a spiral path.

In the "Surface Renewal Model," it is assumed that the mass transport boundary layer in the wake of each particle is replaced by bulk solution (Fig. 10). The width σ of the swath of the boundary layer renewed by a particle is found to depend on particle diameter, but not on boundary layer thickness, as one would expect. The limiting current to an element of the electrode surface increases sharply as a particle passes over it and afterwards decays back to the value corresponding to the undisturbed boundary layer. Particles within a critical interaction distance Δ from the surface are treated as being on the surface. This interaction distance is found from a best fit of experimental results to be quite independent of rotation rate and disk diameter but strongly dependent on particle size (Fig. 11). For the most part, the interaction distance is found to be proportional to the particle diameter d (Fig. 12). A ratio d/Δ of 43 has been used for the computations. This large value indicates that particles have to be very close to the surface to have an effect on mass transfer.

The surface renewal model can reasonably account for the effect of solids content and rotation rate (Fig. 13), but does not correctly predict the effect of particle size (Fig. 14).

In an alternate "Particle Film Model," it is assumed that a liquid film of thickness Δ, which is proportional to the particle diameter, clings to the particle and rotates with it under the influence of the velocity gradient near the surface (Fig. 15). Enriched solution is carried by the rotating particle to the electrode, which is covered by a mass transfer boundary layer of thickness δ, and depleted solution is returned to the bulk solution. The complex interaction of the spherical particle film which rolls over the electrode with the electrode surface, has been simplified assuming transport from three distinct distances from the surface with equal contact time. (1.4%, 12.7% and 114.6% of particle radius) (Fig. 16). Level 0 represents transport from a large liquid volume with a small concentration gradient. Level 2 represents the other extreme, small volume and large gradient. The relative areas of the three levels vary with particle diameter and velocity. They have been chosen for best agreement with experiment. Level 0 predominates for small particles and low velocities, level 2 for large particles and high velocities.

The Particle Film Model explains the observed limiting currents better than the Surface Renewal Model. The comparison of predicted behavior and data points, shown in Fig. 17, illustrates that the representation of the dependence on volume fraction is approximately correct. The predicted dependence on rotation rate changes from parabolic to linear with increasing particle content, in agreement with experiment, but shows some disagreement with measurements (Fig. 18). The principal advantage of the Particle Film Model over the Surface Renewal Model lies in that the former correctly represents the dependence of mass transfer enhancement on particle size. Predictions agree with measurements within experimental error (Fig. 19). Also, the predicted optimum particle size shifts to smaller diameters as the rotation rate is increased. We note that the predicted optimum diameter is somewhat larger than that derived from experiments.

STIRRING POWER

As a measure of the effectiveness of solid particles for enhancing mass transfer to a rotating disk, the computed power dissipation of the disk per unit area has been divided by the measured limiting current density. This ratio, shown in Fig. 20, is a measure of the energy required for stirring per unit reactant. The presence of particles is found to be particularly effective at an intermediate volume fraction and at high rotation rates. Increasing the limiting current by the addition of particles at constant rotation rate requires a much lower increase in stirring power than by increasing rotation rate in the absence of particles (Fig. 21).

CONCLUSIONS

Suspended solid particles moving past electrode surfaces represent an effective means for increasing transport to and from electrode surfaces. Of the two tentative theoretical models developed so far, the Particle Film Model appears to have better physical validity, and it also gives better agreement with experimental data. Before attempting further development of theoretical models, experiments with different particle shapes, and in other flow situations are planned to identify the principal mechanisms by which mass transfer enhancement by suspended particles occurs.

ACKNOWLEDGMENT

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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Table I. Nominal size ranges of beads and their mean diameters based upon volume of beads.

Nominal Size	Volume Mean Diameter
1-5 μm	4.0 μm
5-10	8.4
8-20	13.7
10-25	12.4
44-53	56
61-74	75

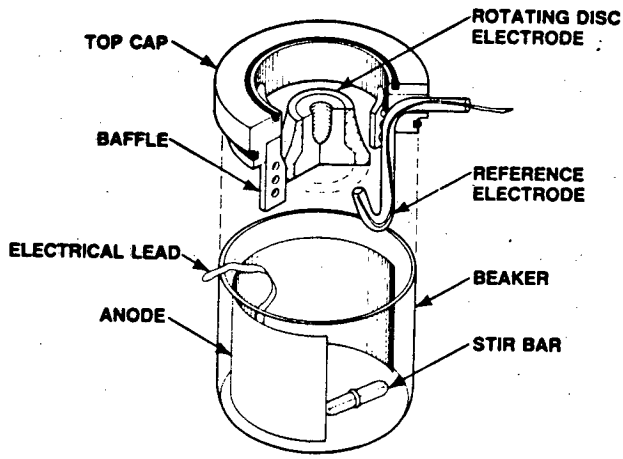

Fig. 1. Cutaway exploded diagram of the experimental cell. The rotating disk electrode is connected to the spindle (not shown) of the rotating disk apparatus.

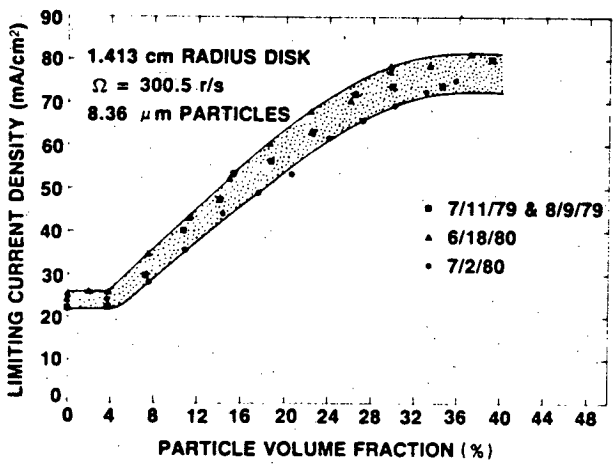

Fig. 2. Reproducibility of experimental limiting current measurements, illustrated by the results of four different experimental runs using the same size (8.36 μm diameter) glass beads. Disk radius 1.413 cm, rotation rate 300.5 rad/s.

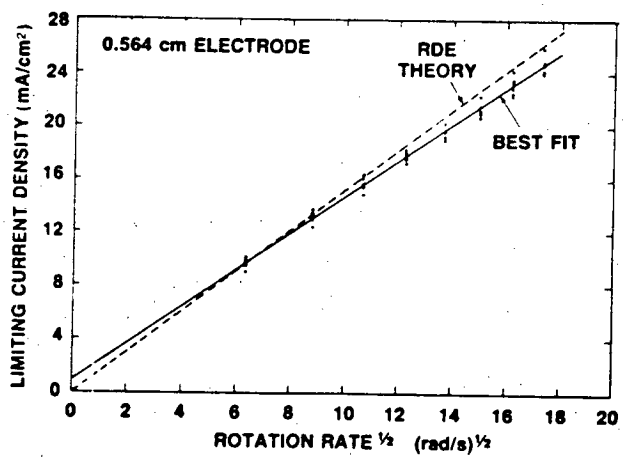

Fig. 3. Dependence of experimental limiting current densities without particles on disk rotation rate. Comparison with limiting current densities calculated by use of the classical rotating disk electrode theory. Disk radius 0.564 cm.

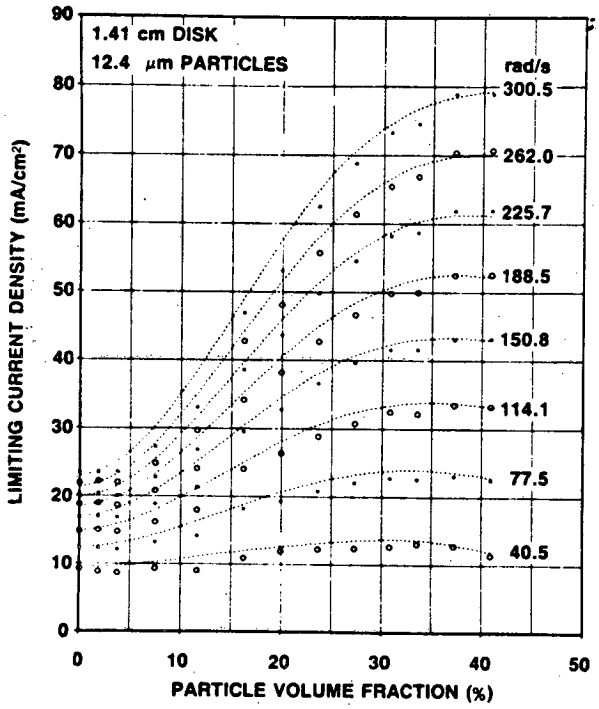

Fig. 4. Dependence of limiting current on volume fraction of particles (12.4 μm diameter) for different disk rotation rates; disk radius 1.413 cm. Experimental data points and cubic spline curves.

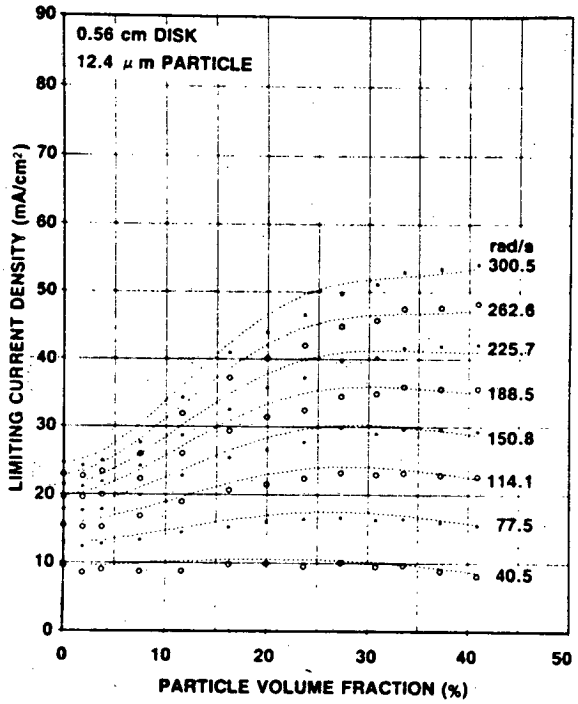

Fig. 5. Dependence of limiting current on volume fraction of particles (12.4 μm diameter) for different disk rotation rates; disk radius 0.564 cm. Experimental data points and cubic spline curves.

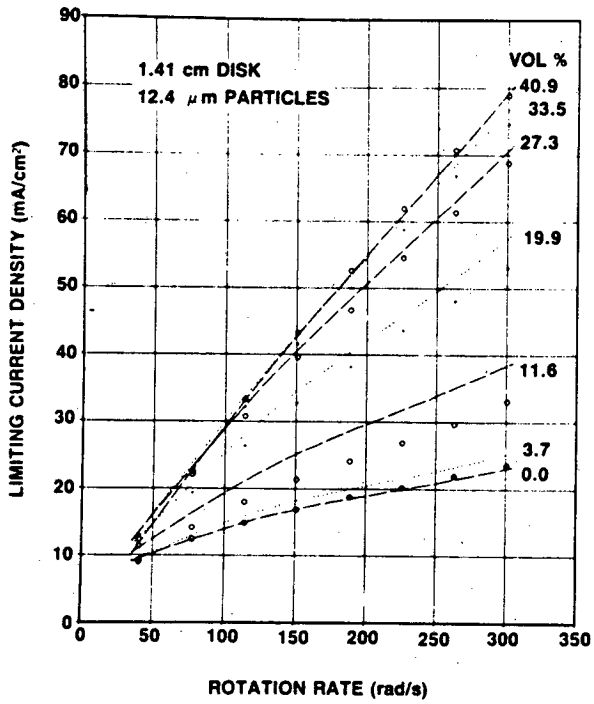

Fig. 6. Dependence of limiting current on disk rotation rate for different volume fractions of particles (12.4 μm diameter); disk radius 1.413 cm. Experimental data points and cubic spline curves.

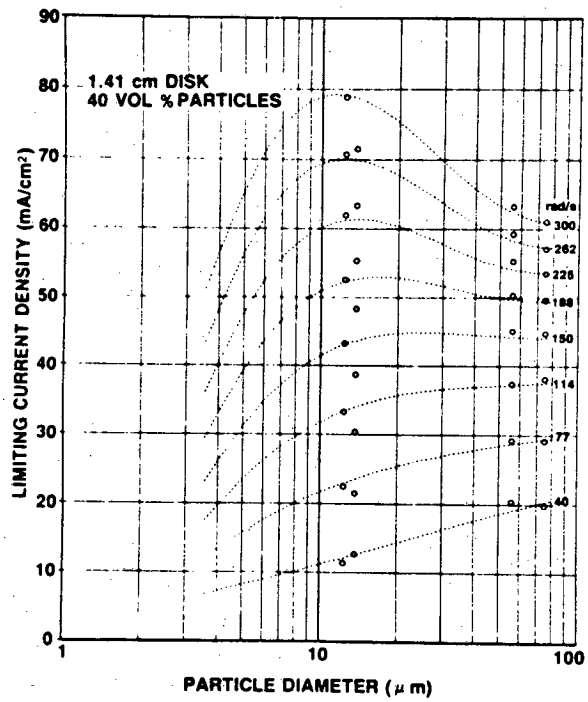

Fig. 7. Dependence of limiting current on particle diameter (at 40 ± 2 vol %) for different disk rotation rates; disk radius 1.413 cm. Experimental data points and cubic spline curves.

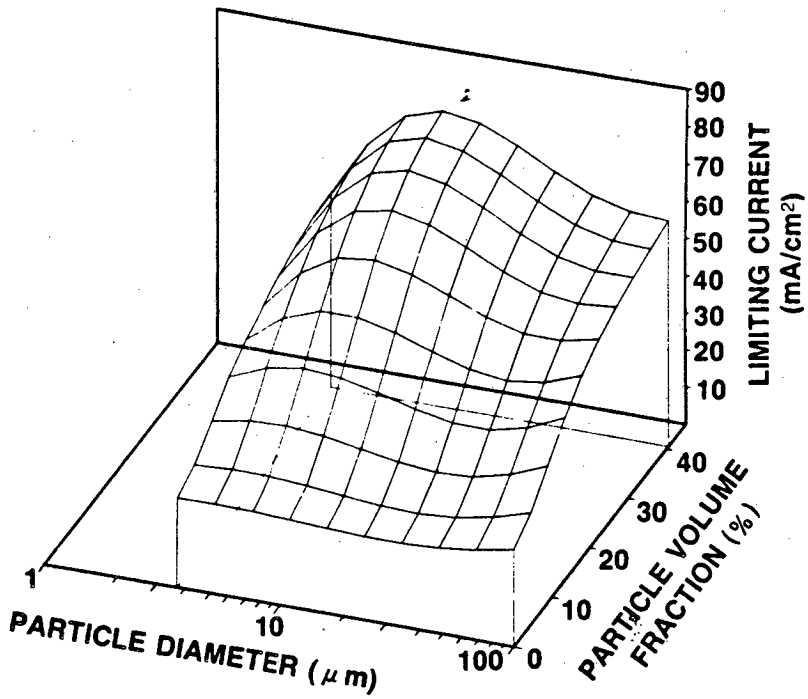

Fig. 8. Dependence of experimental limiting current density on particle diameter and volume fraction as expressed by the cubic spline function. Disk radius 1.413 cm, rotation rate 304 rad/s.

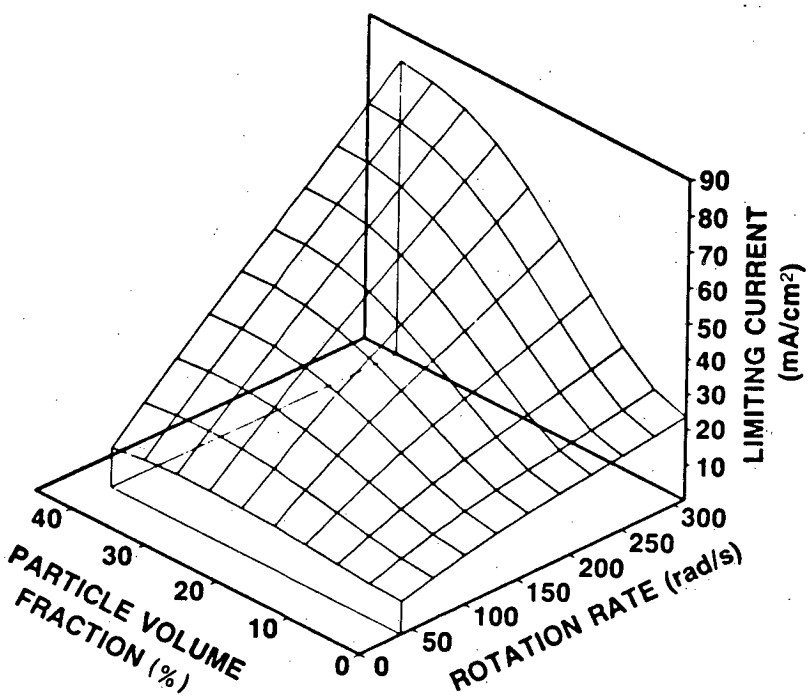

Fig. 9. Dependence of experimental limiting current density on volume fraction and disk rotation rate as expressed by the cubic spline function. Disk radius 1.413 cm, particle diameter 10.7 μm.

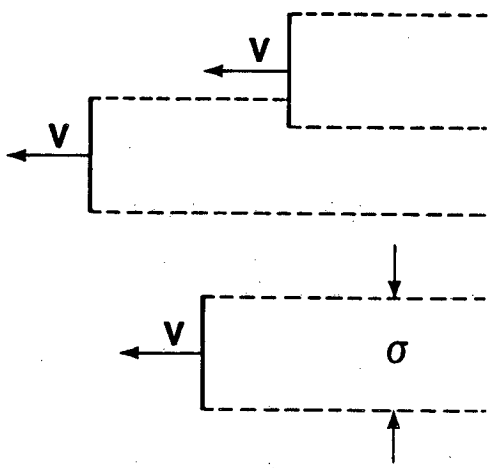

Fig. 10. Surface renewal model. Randomly dispersed particles traveling across the disk surface with uniform velocity V cut swaths of width σ in which the old boundary layer is replaced by fresh bulk solution.

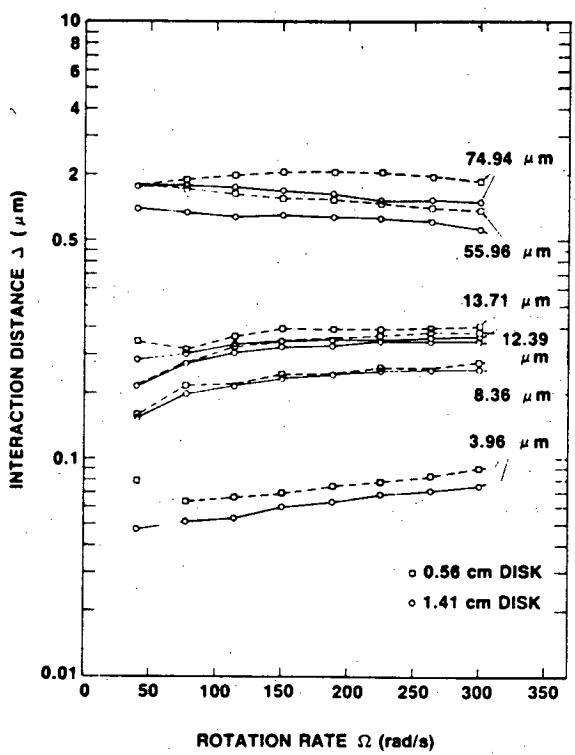

Fig. 11. Interaction distances, Δ, which yield least squares fits of surface renewal model to observed limiting currents, for different particle sizes and disk radii.

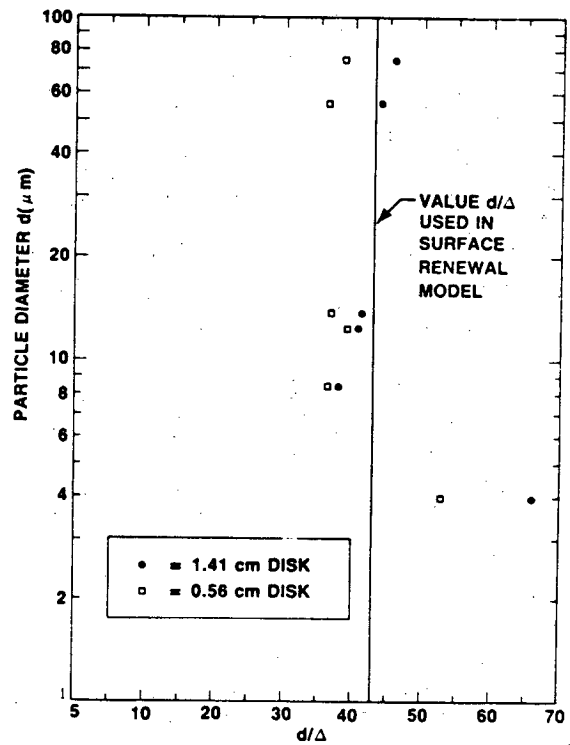

Fig. 12. Interaction distance Δ for the surface renewal model and particle diameter d for best agreement with experiment. The mean value (d/Δ = 43) is used in Figures 13 and 14.

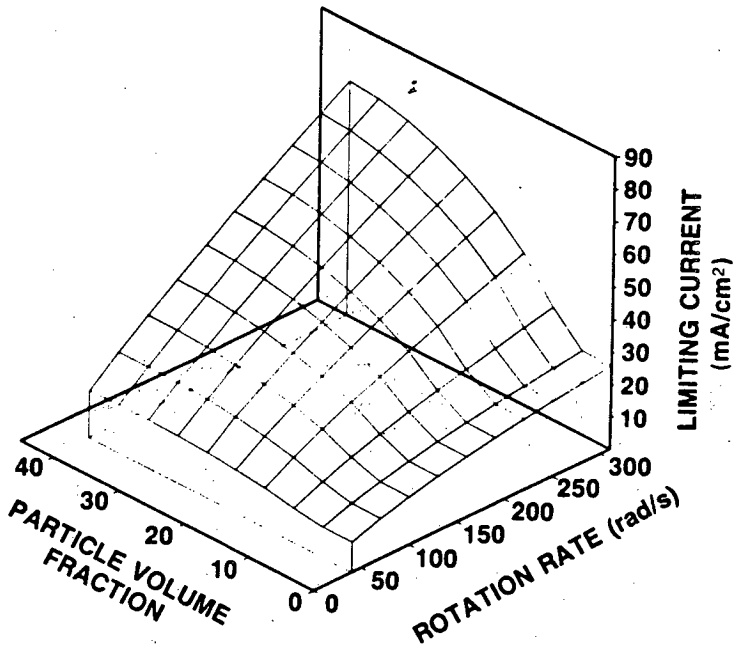

Fig. 13. Dependence of limiting current density on particle volume fraction and disk rotation rate as predicted by the surface renewal model. Disk radius 1.413 cm, particle diameter 10.7 μm. (Measurements shown in Figure 9.)

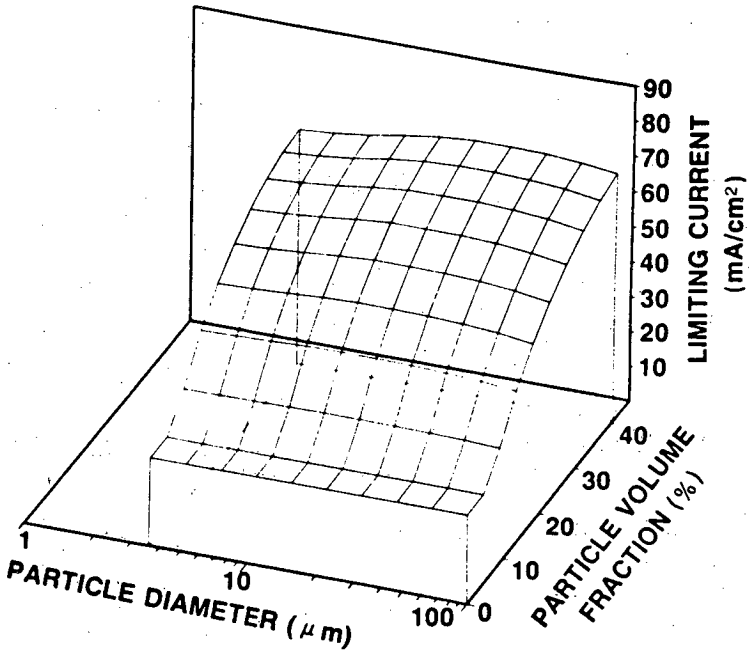

Fig. 14. Dependence of current density on particle diameter and volume fraction as predicted by the surface renewal model. Disk radius 1.413 cm, rotation rate 304 rad/s. (Measurements shown in Figure 8.)

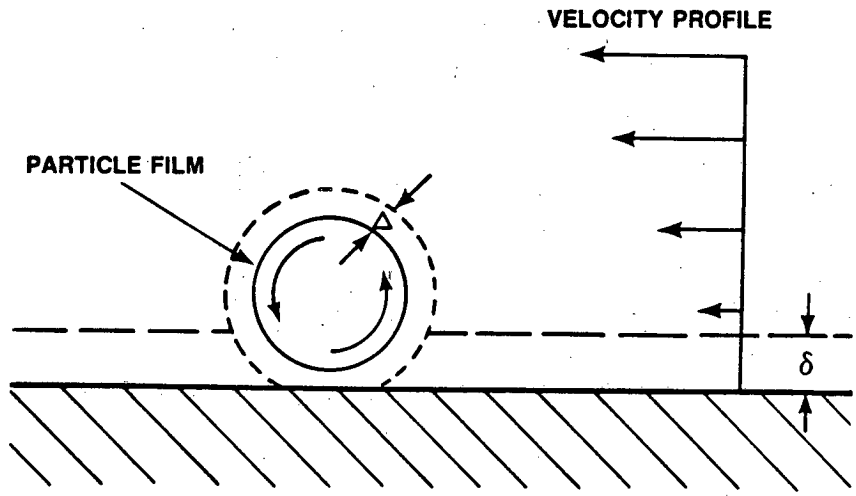

Fig. 15. Particle film model. Particle surrounded by a film of solution (thickness Δ) rolling over the electrode (boundary layer thickness δ) under the influence of a velocity gradient.

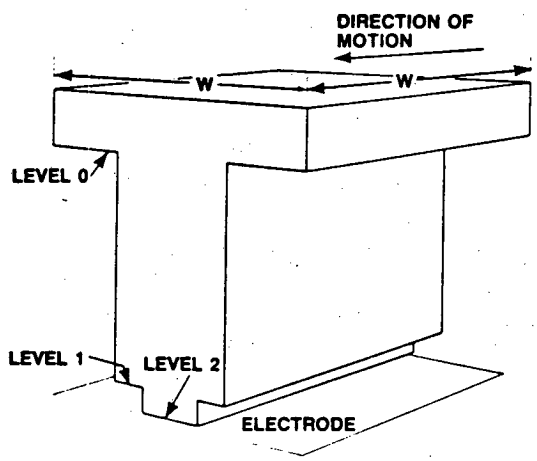

Fig. 16. Simplification for the continuously variable distance of interaction between a rotating sphere and the electrode surface for the particle film model.

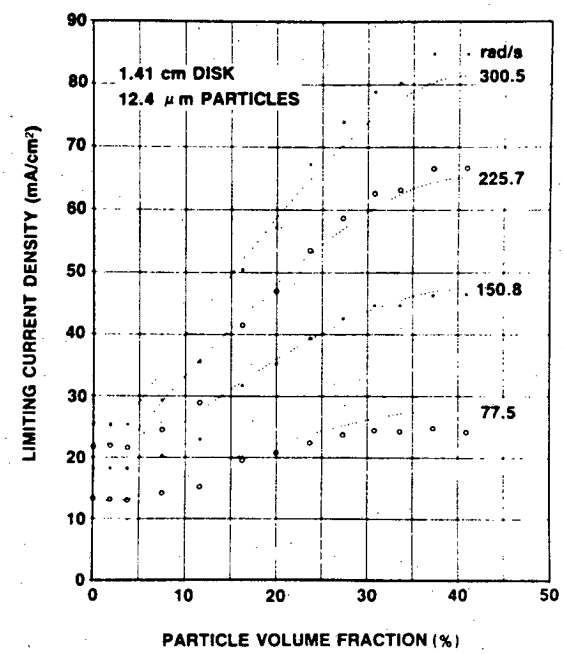

Fig. 17. Dependence of limiting current on volume fraction of particles (12.4 μm diameter) for different disk rotation rates; disk radius 1.413 cm. Prediction by the particle film model and experimental data points.

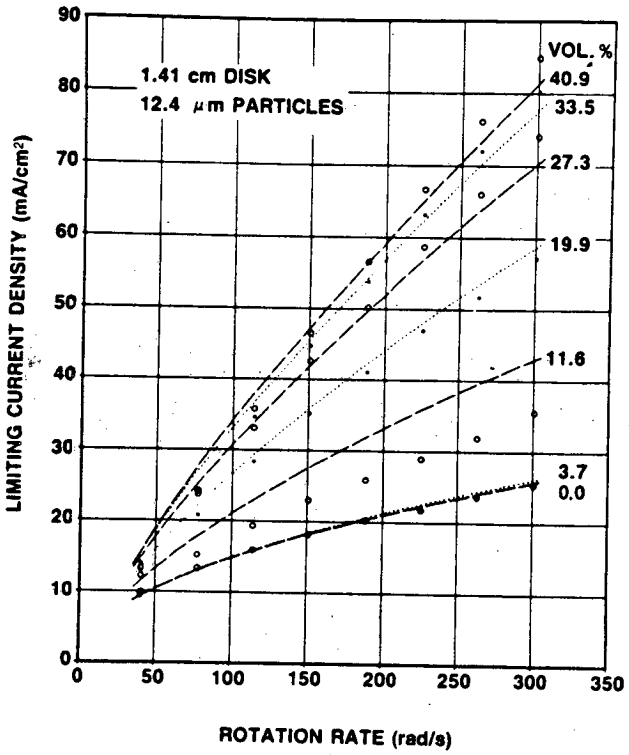

Fig. 18. Dependence of limiting current on disk rotation rate for different volume fractions of particles (12.4 μm diameter); disk radius 1.413 cm. Prediction by particle film model and experimental data points.

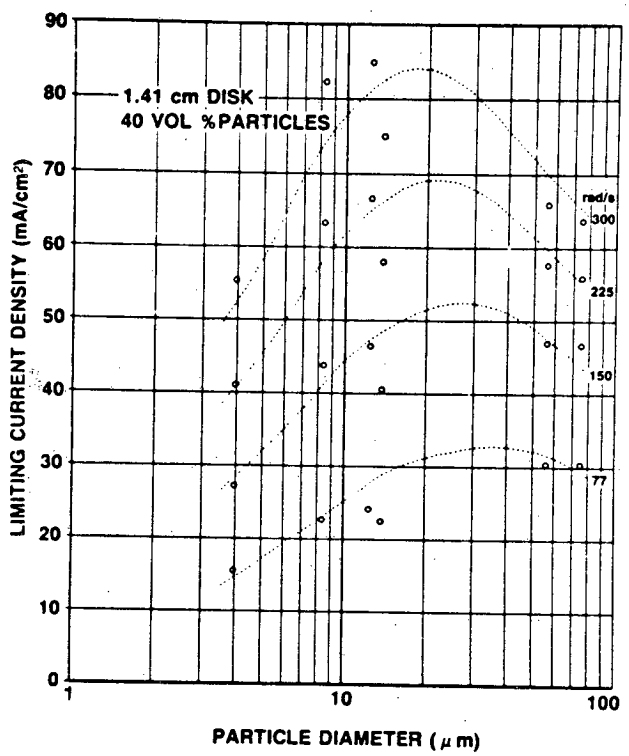

Fig. 19. Dependence of limiting current on particle diameter (40 ± 2 vol %) for different disk rotation rates; disk radius 1.413 cm. Prediction by particle film model and experimental data points.

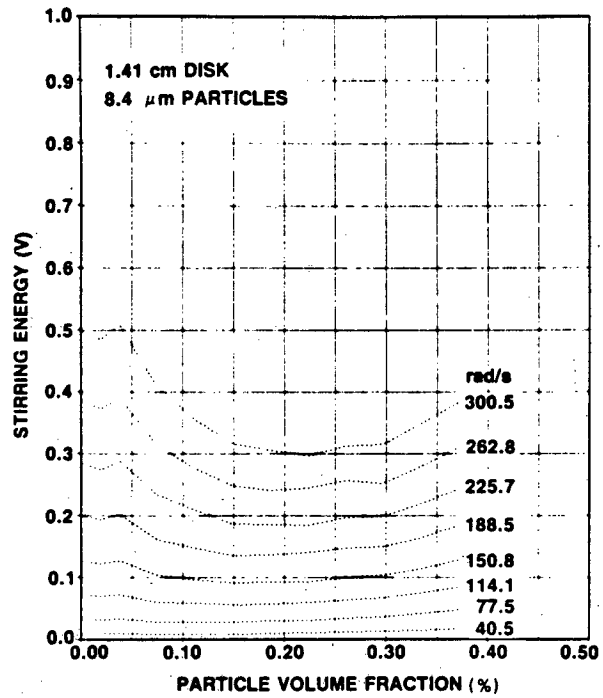

Fig. 20. Stirring energy for mass transport per unit reactant, obtained by dividing the agitation power (watts/cm^2) by the limiting current density (A/cm^2) as a function of the volume fraction of particles for different disk rotation rates. This quantity represents the minimum energy to effect mass transfer per unit reactant. Disk radius 1.413 cm, particle diameter 8.4 μm.

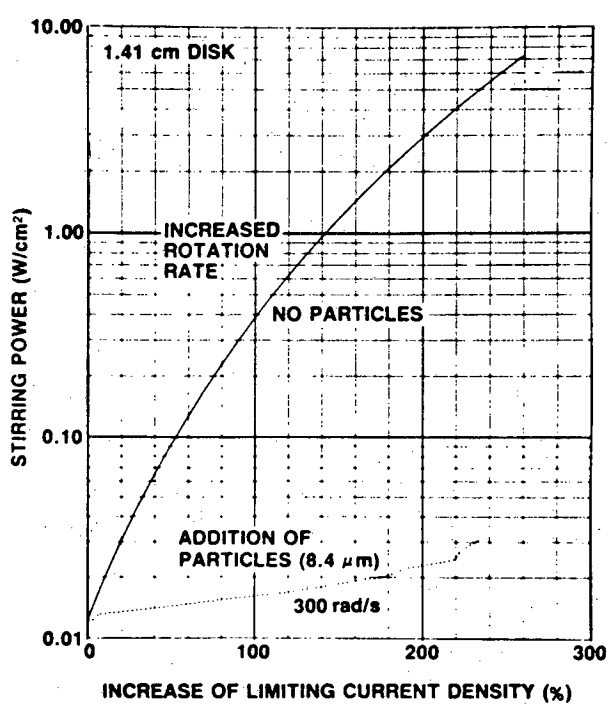

Fig. 21. Stirring power required to increase limiting current by the addition of particles (8.4 μm diameter) at constant disk rotation rate (300.5 rad/s, 1.413 cm radius) compared to increase of rotation rate to achieve the same increase in limiting current without particles.

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