

LETTERS

Ultrafast Chronoamperometry of Acoustically Agitated Solid Particulate Suspensions: Nonfaradaic and Faradaic Processes at a Polycrystalline Gold Electrode

Neil V. Rees, Craig E. Banks, and Richard G. Compton*

Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, United Kingdom

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“Nanosecond” electrochemistry is used to investigate the impacts of various solid particles (alumina and graphite suspended in aqueous perchloric acid and copper suspended in aqueous sodium perchlorate) at a polycrystalline gold electrode under insonation. Current spikes of microsecond duration, attributed to individual impacts, are observed under potentiostatic conditions, with a polarity that inverts at the potential of zero charge of the electrode/electrolyte system. It is found that there is no significant change in the magnitude of these transients as the sizes of alumina particles range from 0.3 to 25 μm . However, appreciable changes are observed in the transients when using electroactive particles, specifically graphite powder surface modified with adsorbed *N,N'*-diphenyl-1,4-phenylenediamine, and evidence is presented for the occurrence of electron transfer during the impact event which occurs on the sub-microsecond time scale.

Introduction

The interaction of particles with surfaces has been of fundamental interest for some time, but the time-resolved direct measurement of individual interaction events has only lately become attainable and electrochemistry has provided a convenient experimental technique for doing so.^{1,2} Recent interest has focused on the adhesion processes of particles, for the importance in industrial applications such as xerography, paints and coatings, and so forth, including clay particles on mercury electrodes.² Interactions between colloidal particles with electrodes have also been studied, commonly with the aim of observing the redox activity of a species within the micellar phase.^{3–7} There has also been some work in the field of nonrigid particles such as liposomes,⁸ biological cells, and oil droplets,^{1,9} including biphasic synthesis.^{10,11}

In an earlier publication, we used a fast potentiostat capable of voltage scan rates of 2.2 MV s^{−1} to investigate the impact

events of heptane and decane droplet emulsions in an aqueous sonoemulsion on the sub-microsecond time scale and found that characteristic current–time transients are produced by these interactions.¹ The transients were found to have a polarity that was dependent on the applied potential, with an inversion point coincident with the accepted potential of zero charge (pzc) for polycrystalline gold and platinum electrodes.

In this communication, we report further results obtained using the same methodology of combining an ultrafast-scan potentiostat (with nanosecond response) with ultrasound to record for the first time the collisions of *solid* particles, suspended in aqueous solution, with polycrystalline gold electrodes. First, a range of electroinactive solid particles are used to probe the possibility of measuring the pzc of the gold electrode, as is possible with the droplets formed via acoustic emulsification, and how the particle size may affect the observed current transients. Second and most importantly, redox-active particles are used to demonstrate that faradaic electron transfer may occur during the sub-microsecond time scale of the particle–electrode collision.

* To whom correspondence should be addressed. Phone: +44 (0)1865 275 413. Fax: +44 (0)1865 275 410. E-mail: richard.compton@chemistry.ox.ac.uk.

Experimental Section

Reagents. The chemical reagents were obtained from commercial sources and used as received without further purification. These were decane (Aldrich, 99+%), alumina (Buehler Ltd., various grades), perchloric acid (Fisher Scientific, 70%), graphite powder (Aldrich, <20 μm), copper powder (BDH, <100 μm), and *N,N'*-diphenyl-1,4-phenylenediamine (DPPD, Aldrich 98%). Experiments were conducted at a temperature of 293 ± 2 K. Dilute acid solutions were prepared using UHQ grade water with a resistivity of no less than 18 M Ω cm (Elga, High Wycombe, Bucks, U.K.).

Instrumentation and Microelectrodes. The potentiostat used was built in-house, has a scan rate of 2.5×10^6 V s $^{-1}$, and was used with a gain of either 2.95×10^3 or 2.95×10^4 Ω and minimum filtering. This potentiostat is essentially that described and utilized by Amatore and co-workers^{12,13} and has a rise time of 10 ns which is sufficient for monitoring chronoamperometric signals for cavitation or related activity in aqueous solution which can occur over a time scale as small as 200 ns. The potential was applied with a TTI TG1304 programmable function generator (Thurlby Thandar Instruments Ltd, Huntingdon, Cambs, U.K.) and the current recorded with a Tektronix TDS 3032 oscilloscope (300 MHz band-pass, 2.5 GS/s). A 20 kHz ultrasound horn transducer system (Sonics & Materials, VCX400) with a stepped 3 mm microtip (titanium alloy, Jencons, Leyton Buzzard, U.K.) was employed. The ultrasonic power was determined calorimetrically according to the procedure of Margulis et al;^{14,15} an intensity of "11%" was found to correspond to 260 W cm $^{-2}$. The horn probe was used in a face-on geometry^{16,17} to the working electrode and positioned at a constant distance of 8 mm.

The microdisk electrode was fabricated by fusing gold wire (99.95%, Johnson Matthey plc, London, U.K.) into soda glass according to a literature method,¹⁸ and the working surface was ground and polished to a mirror finish. A working radius (r_d) of 100 μm was confirmed by electrochemical calibration. Since prolonged sonication can cause erosion of metal microdisk electrodes,¹⁹ care was taken to renew the electrode surface between experiments to ensure experimental consistency. Therefore, the electrode was lightly ground using fine carborundum paper and polished using ultrapure water and appropriate grades of alumina slurry on soft lapping pads, and then, it was finally rinsed in ultrapure water and dried carefully. The counter electrode was a smooth, bright, platinum mesh, and a palladium spade (99.95%, Advent Research Materials Ltd, Eynsham, Oxon, U.K.) charged with hydrogen in a separate compartment was used as a reference electrode.¹

Results

1. Graphite Powder. For these experiments, ~ 200 mg of graphite powder (with a diameter distribution between 2 and 20 μm) was added to 15 mL of 0.10 M perchloric acid solution, and this was sonicated to obtain a suspension. The selected potential was applied and sonication continued. As reported for the case of heptane and decane, significant current spikes were observed at the set potential with durations of < 10 μs .¹ The potential was then changed, and further recordings were made. The polarity of the current spikes was observed to change at a potential of -5 ± 5 mV (vs Pd/H $_2$), with negative currents shown at potentials negative of the transition potential and positive currents at potentials positive of the transition potential, as illustrated in Figure 1. The variation in the charge displaced (ΔQ) obtained from integration of the peaks is given in Figure 2. The frequency of transients was estimated at $> 10^3$ s $^{-1}$ and

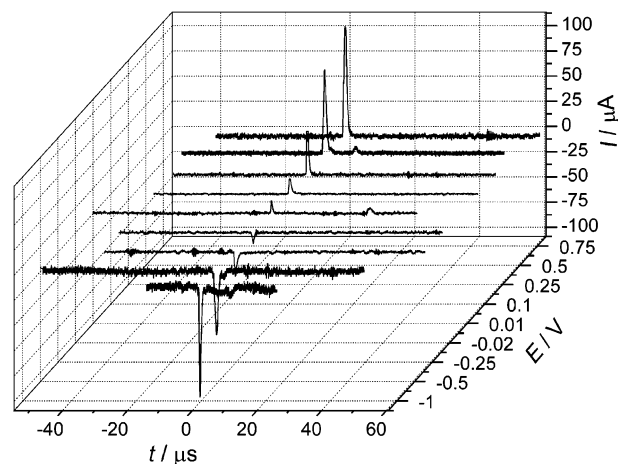


Figure 1. Current transients recorded for graphite powder under sonication at different potentials.

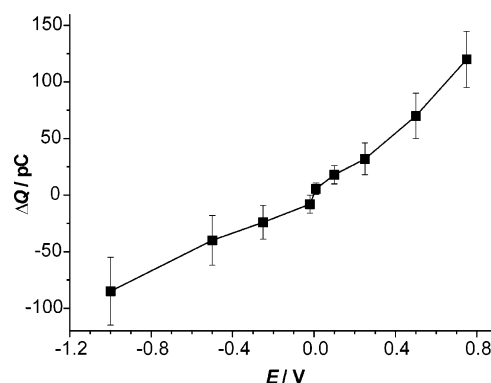


Figure 2. Plot of the charge displaced (ΔQ) by impact events as a function of potential for graphite powder.

was observed to increase as more graphite powder was added to the suspension. The transition potential corresponds to 0.128 ± 0.010 V (vs the standard hydrogen electrode (SHE)) which agrees well with reported values for the pzc for polycrystalline gold in this medium of 0.10–0.14 V versus SHE.^{1,20,21}

2. Alumina Powder. Analogous experiments were conducted with ~ 250 mg of different sizes of alumina powder (particle diameters of 0.3, 9.5, and 25.0 μm) in 15 mL of 0.10 M perchloric acid solution. Current transients were observed under sonication which shows an inversion of polarity at the same transition potential as above, as illustrated in Figure 3. The transition potential was found to be unaffected by the size of alumina particles employed. The charge displaced (ΔQ) by the particle impacts, corresponding to the time-integrated current spike, was also found to be approximately independent of particle size over the range studied here, as shown in Figure 4. This indicates that the impact area must be sufficiently small such that there is no significant difference in impact area over this range of particle sizes. The observation that the ΔC value is smaller than that for graphite may indicate the lower conductivity of the solid.

3. Copper Powder. The above results for graphite and alumina powders do not conclusively exclude the possibility that the measured pzc is that of the particle and not the gold surface. The reported pzc for graphite ($+0.115$ V vs SHE²²) lies in the same region as that for polycrystalline gold ($+0.10$ to $+0.14$ V vs SHE).

To show that the pzc of the electrode is measured by our method, we conducted experiments with ~ 250 mg of copper powder (particle diameters of < 100 μm) in 15 mL of 0.10 M

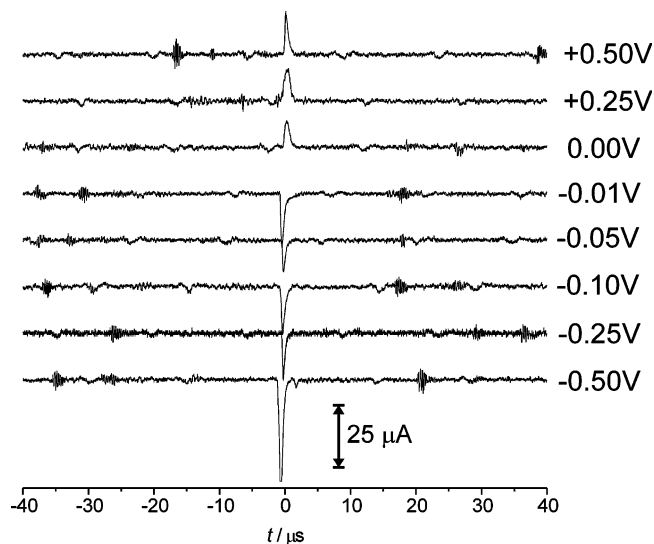


Figure 3. Current transients recorded for 25.0 μm alumina powder under sonication at different potentials.

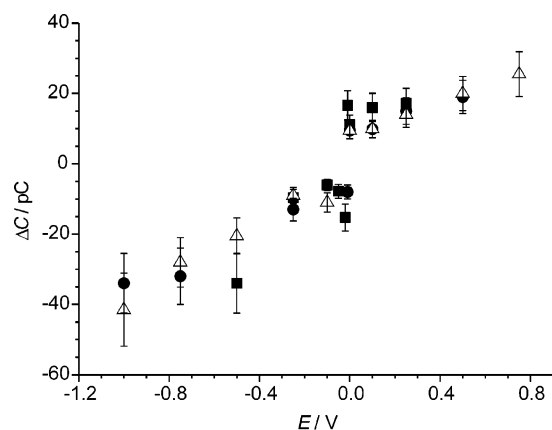


Figure 4. Plot of the charge displaced by impact events as a function of potential for alumina particles of the following sizes: 0.3 μm (Δ), 9.5 μm (\bullet), and 25.0 μm (\blacksquare).

sodium perchlorate solution. The pzc for polycrystalline copper in 0.10 M $\text{NaClO}_4(\text{aq})$ has been reported to be -0.73 V (vs SHE).²³ The copper was cleaned of any surface oxides prior to use by immersion in dilute nitric acid solution and rinsing in pure water. Under sonication, current transients were again observed which had an inversion of polarity at the same transition potential as above, that is, -5 ± 5 mV (vs Pd/H_2). Figure 5 shows a sample of current transients as a function of applied potential. We conclude that the transient inversion potential (E_{inv}) therefore relates to the pzc of the electrode material and not to that of the incident particle. The sizes of the transients are up to 5 times larger than those for graphite, and the increased charge displaced can again be qualitatively explained by the increased conductivity of the particle.

4. Faradaic Electron Transfer during Impact Events: *N,N'*-Diphenyl-1,4-phenylene-diamine Derivatized Graphite Powder (DPPD/C). First, DPPD is adsorbed onto the graphite by stirring a 10 mM solution of DPPD in water with the graphite powder for 2 h at room temperature, followed by filtration and drying.²⁴ The derivatization of the graphite powder was confirmed by abrasively immobilizing a small amount of DPPD/C on a 3 mm basal plane pyrolytic graphite (BPPG) electrode and measuring its voltammetry in 0.10 M perchloric acid. This is shown as inset a in Figure 6, with inset b displaying the diffusion-only cyclic voltammogram of a solution of DPPD

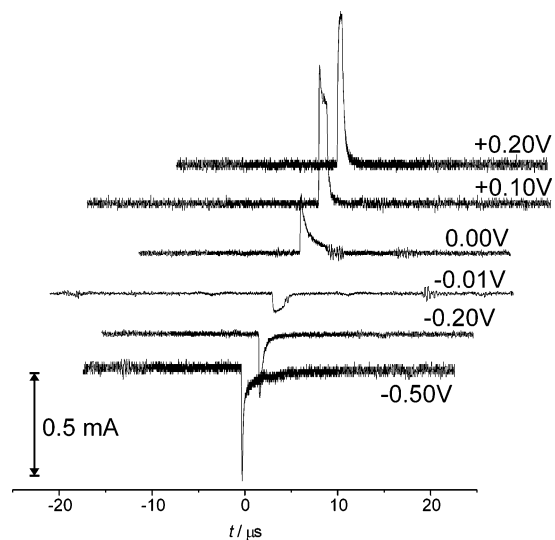


Figure 5. Current transients recorded for copper powder under sonication at different potentials.

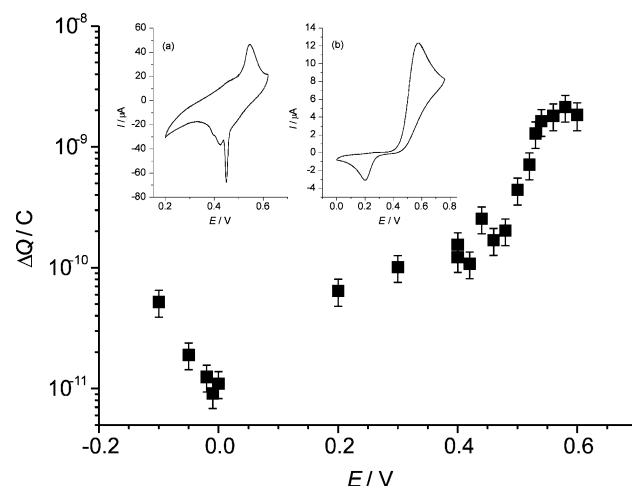


Figure 6. Logarithmic plot of the charge displaced by DPPD/C particle impacts as a function of potential. The insets show cyclic voltammograms of (a) DPPD/C powder immobilized on a 3 mm BPPG electrode in 0.10 M $\text{HClO}_4(\text{aq})$ and (b) a solution of DPPD in 0.10 M $\text{HClO}_4(\text{aq})$ recorded at the 100 μm gold electrode.

in 0.10 M perchloric acid recorded at the 100 μm gold disk electrode.

Next, ~ 200 mg of DPPD/C powder was added to 15 mL of 0.10 M perchloric acid solution, and this was sonicated to obtain a suspension. Initial transients were recorded at negative potentials, and the transition potential for the inversion in transient polarity was once more observed at -5 ± 5 mV. Upon moving to more positive potentials, the (oxidative) current transients were observed to be of the same order of magnitude as previous experiments with electrochemically inactive graphite particles. However, upon further increasing the potential, a sudden increase in the magnitude of the current transients was seen which corresponded to the first oxidation wave of DPPD (see Figure 6 and insets). This was consistently observed for further recordings taken at $E > 0.40$ V, with at least a 1 order of magnitude increase in the integrated area of the transient spike. Figure 6 shows this effect on the charge passed by each impact.

Discussion

The above results empirically show a good correlation between the transient inversion potential (E_{inv}) and the pzc of

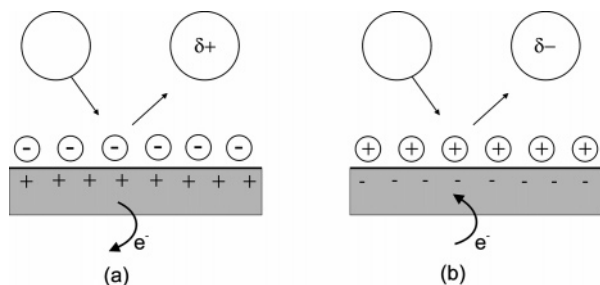


Figure 7. Schematic diagram of the process postulated to occur during particle impact where (a) the electrode is positive of the pzc and (b) the electrode is negative of the pzc.

polycrystalline gold in perchloric acid. In the absence of faradaic processes, at potentials both positive and negative of E_{inv} , charges in the range 10^{-10} – 10^{-12} C are injected during the transient, which is in good agreement with the results reported for alkane droplet impacts.¹ The total charge carried on the electrode is likely to be $\sim 200 \mu\text{C cm}^{-2}$,²⁵ corresponding for a $100 \mu\text{m}$ electrode to a charge of $\sim 6 \times 10^{-9}$ C, and is therefore at least a factor of 50 times in excess of those recorded. This is consistent with the finding that there is no significant effect on the charge passed during impact due to the particle size (in the range 0.3 – $25 \mu\text{m}$), and together, these observations suggest that the impact area is submicron in size and most of the electrode/electrolyte impact remains unperturbed by the impact.

We also note that each transient is unidirectional, indicating that charge neutrality is maintained via a counter electrode process. This observation is again consistent with an impact event where the colliding particle removes charge from the electrode–electrolyte interface without penetrating deeply. If the particle remained long enough in contact with the electrode to “block” it, a reverse transient would be expected as the charge was recovered by the double layer when the particle left. A pictorial representation of the process is given in Figure 7.

Conclusions

We have shown that particulate suspensions can be used with ultrasound to determine the pzc of solid electrodes, as an alternative to the use of sonoemulsified heptane or decane droplets.¹ Most significantly, electron transfer has been observed during the collision of electroactive solid particles with the electrode. These faradaic processes will be further examined in subsequent work, with reference to possible analytical and fundamental applications.

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Note Added after ASAP Posting. This letter was released ASAP on November 9, 2004. Sentence 3 has been revised in paragraph 1 of the Discussion section. The correct version was posted on November 10, 2004.

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