**Electrochemistry**

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# A Method for the Positioning and Tracking of Small Moving Particles[**]

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The nonperturbing tracking of particles in a liquid, that is, the precise quantification of their position as a function of time, is both challenging and of great importance, for example, in following the motions of viruses or bacteria, as well as for underpinning advances in nanotechnology such as the development of nanomotors.[1] Of course, microscopes and optical methods have long been used but are limited to where sample irradiation is both possible and noninvasive. Accordingly, we have sought to develop a new approach for the tracking of small particles based on electrochemical methods (for an introduction see Ref. [2]). Herein, we demonstrate for the first time the ability to locate a particle in space–time by using a simple array comprising individually addressable electrodes.

The background to this work lies in the sizing and characterization of small (that is, sub-millimeter) particles, which is commonly achieved by using methods such as electrical sensing zone and laser diffraction.[3,4] Recent work has demonstrated that solution-based electrochemical methods are capable of performing the same function under certain conditions.[5–8] To date, potential-step chronoamperometry has been used to size stationary particles under "dark" and photochemical conditions,[5,6] and to simultaneously size and locate a sphere.[6,7] These techniques require an electroactive species in solution and rely on the disruption by the particle of the diffusional field around one or more microelectrode detectors. This disruption alters the current response, which can then be interpreted by either computation[5,6] or experimental calibration.[7] In dynamic systems, the use of ultrasound has enabled the electrochemical sizing of spherical particles,[8] this technique is based on the established property of the creation of (non-Faradaic) current spikes by particles that collide with an electrode.[9–11] Whilst an advantage of this sono-electrochemical method is that no electroactive species is required to be present in order to size the particles, the ultrasound power can be destructive.

No attempt to measure the motion of a particle by using electrochemical methods has been reported to date. However, we demonstrate for the first time the ability to track a particle moving in the solution phase in both time and two-dimensional space by sing a simple electrode array and potentiostat. The work represents proof-of-concept; with a view to the future we note that electrochemical methods are capable of sub-micrometer spatial and sub-microsecond temporal resolution.[12,13]

It is known that a stationary sphere placed close enough to an electrode in the presence of an electroactive species will affect the current response of the electrode.[5,7] We first performed calibration experiments with a basalt sphere and the electrode array. A solution containing ferrocene (3.8 mM) and tetra-*n*-butylammonium perchlorate (TBAP; 0.1M) in acetonitrile was placed in the cell, together with a single sphere of diameter 330 μm. For these calibration experiments, the stepper motor was switched on in order to exactly match the conditions of the moving-sphere experiments, as this caused some mechanical vibration of the cell and solution. The magnet was therefore removed from the cell assembly to ensure no translational motion of the sphere occurred. The ball was positioned and chronoamperograms were recorded at each electrode. The potential was stepped from 0.25 V to 0.75 V (versus Ag) for 2.5 s to effect the oxidation of ferrocene. The resulting chronoamperograms were analyzed to extract current values for times of 0.5, 1.0, 1.5, 2.0, and 2.5 s after the potential step. A photograph was taken to confirm the actual position of the ball. This process was repeated for many different positions of the sphere to yield calibration plots that relate the observed current to the centre–centre displacement between the sphere and the electrode. It was noted that the presence of the sphere is only detectable within a distance of approximately 0.5 mm for the present combination of ball and electrode sizes. The calibration plot for $t = 2.5$ s is shown in Figure 1 (the remaining calibration plots are shown in Figure S1 in the Supporting Information).

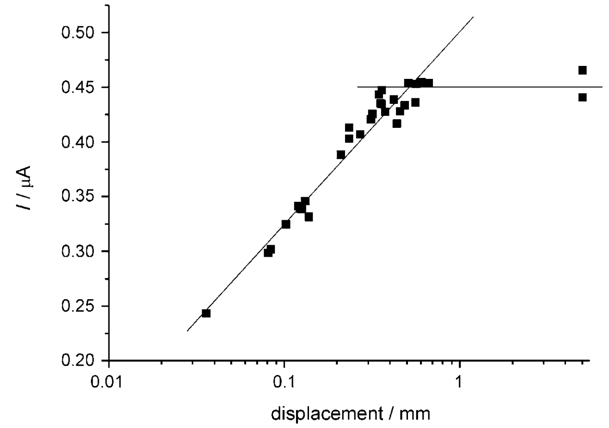

***Figure 1.*** A typical calibration plot of transient current vs. displacement (centre of sphere to centre of electrode) for stationary spheres at a time of 2.5 s immediately following a positive potential step (more plots of this type are provided in the Supporting Information.

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The magnet was subsequently replaced in its carriage and the stepper motor was switched on. A square-wave potential trace was applied, and the magnet moved smoothly beneath the glass plate containing the array whilst the video footage of the electrodes was recorded. The basalt sphere was observed to move across the square array by following the magnet in a series of short hops (a typical current–time response is shown in Figure 2).

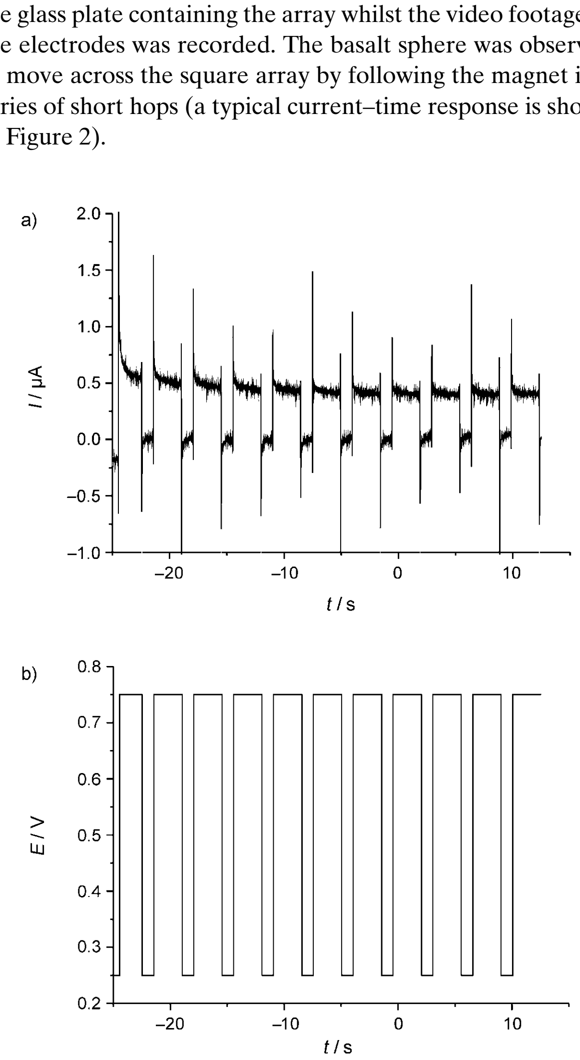

*Figure 2.* a) A typical current–time response, together with b) the applied square wave potential trace for a moving-sphere experiment. Note that the timescale is arbitrary.

To analyze each of these transients, the current was determined at 0.5, 1.0, 1.5, 2.0, and 2.5 s after each positive potential step and compared to the appropriate calibration plot (see Figure 1 and Figure S1 in the Supporting Information) to convert the current response into a spatial displacement. Calculations indicate that the motion of the sphere has an associated Reynolds number of less than 100,[14] we therefore assume that the movement of the sphere does not create significant stirring of the solution,[13] this assumption is supported by experimental observation.

The video was independently analyzed on a frame-by-frame basis to determine the actual path of the sphere and make measurements of its displacement from each of the four electrodes during its movement. Visual and electrochemical displacement measurements could then be compared as shown in Figures 3 and 4, which both demonstrate an excellent correlation.

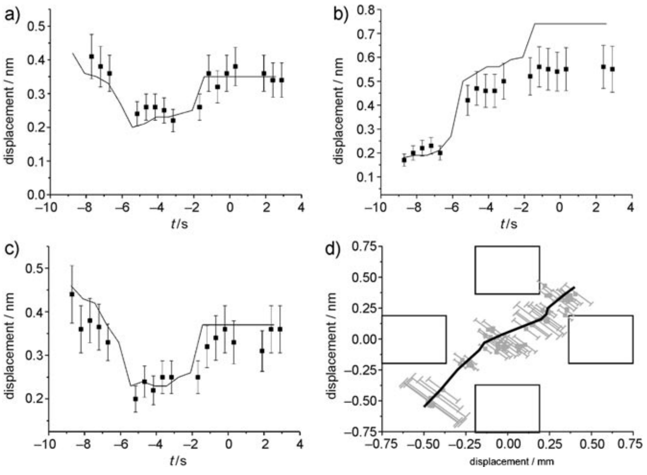

*Figure 3.* Results of ball-moving experiments using video (——), and electrochemical (■) analysis to determine the ball trajectory. a)–c) Displacement–time plots for three different electrodes in the array. d) Overall path of the sphere superimposed on a schematic representation of the electrode array, where the electrochemical data points are in grey for clarity. Note the electrodes cannot respond to displacements greater than approximately 0.55 mm for this combination of electrode and sphere size (see text), and the arbitrary timescale.

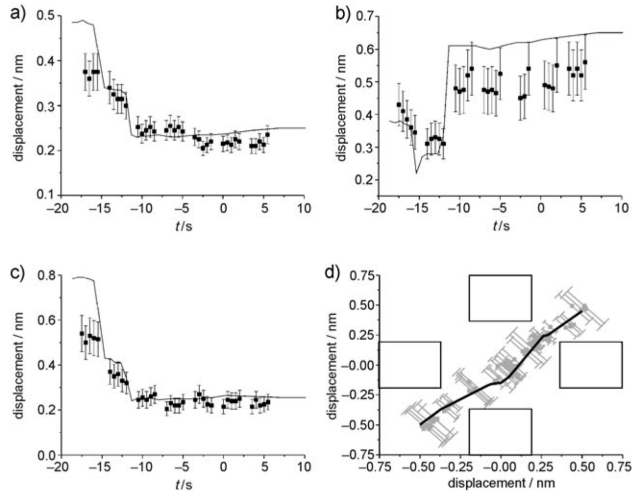

*Figure 4.* As for Figure 3, but for a separate ball-moving experiment.

It is therefore possible to monitor the motion of a moving sphere across an individually addressable electrode array to a high level of accuracy in both time and spatial dimensions. Future avenues of enquiry will include improving resolution to enable the spatial and temporal sensitivity of the experiment to below the microscale, investigating the effects of both array and sphere size, and extending the method to the study of solution-borne objects (that is, monitoring Brownian motion rather than rolling motion along a plane). In this way, the height of the electrode above the glass wafer should not create an obstacle to the microscale object as it would if it were rolling along the wafer. Any increase in the number of array elements will have an effect on the interaction of the diffusion fields, as has been thoroughly investigated previously.[15–19] Significant improvements in the sensitivity of this technique will present numerous challenges, for example in the calibration of the array response. Whilst we are optimistic that such issues can be resolved, such as the problem of calibration can be solved in principle by computer simulation of the current response, the practical difficulties of increasing the spatial sensitivity by two orders of magnitude should not be underestimated.

## Experimental Section

Ferrocene, tetra-*n*-butylammonium perchlorate (TBAP), and acetonitrile were all used as received without further purification. The basalt spheres were of size distribution 300–355 μm in diameter, with a magnetite content of approximately 15 %. The magnets (diameter 1.5 mm) were of NdFeB alloy and were obtained commercially.

An array of four gold microelectrodes on a glass wafer (0.5 mm thickness) was prepared by using standard photolithographic procedures.[20,21]

A μAutolab Type I potentiostat was used for the electrochemical calibration measurements. Moving-ball experiments were conducted using a multichannel potentiostat, built in-house, and controlled using a programmable function generator with data output to an oscilloscope. A bright platinum wire and a silver wire were used as counter- and reference electrodes respectively.

The electrochemical cell was formed by sealing a glass cylinder onto the glass plate containing the microelectrode array. The glass plate was then rigidly clamped approximately 0.5 mm above the magnet which was housed in a carriage mounted on a screw-thread. A 12 V stepper motor was used to rotate the screw-thread, which provided a smooth movement of the magnet carriage beneath the array. The experimental setup is shown schematically in Figure 5. Still photographs and videos (recorded at 30 fps) were obtained using a microscope with electronic eyepiece.

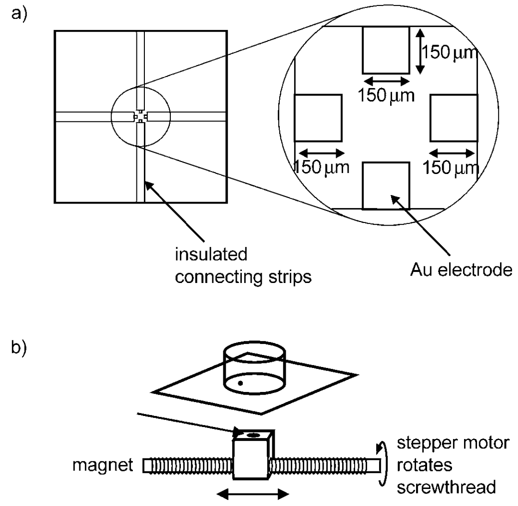

*Figure 5.* Schematic diagram showing a) the electrode array and b) the method for moving the magnet beneath the array and cell.

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