

Sonoelectrochemistry Understood via Nanosecond Voltammetry: Sono-emulsions and the Measurement of the Potential of Zero Charge of a Solid Electrode

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“Nanosecond” electrochemistry is used to study acoustically emulsified mixtures of aqueous electrolyte and smaller quantities of heptane. Significant current spikes of microsecond duration are observed under potentiostatic conditions and attributed to the impacting of heptane droplets onto the electrode surface. The polarity of the transients is found to change as the electrode potential varies through the accepted potential of zero charge of the electrode/electrolyte system for both gold and platinum electrodes. A possible explanation is suggested and the implications for a generic approach to the experimental measurements of potentials of zero charge (pzc) of solid electrodes noted.

Introduction

The potential of zero charge (pzc) of an electrode–electrolyte interface is of immense fundamental significance and its knowledge is intrinsic to understanding and modeling the nature of the interfacial double layer.^{1–3} The determination of the pzc has received much attention over the past decades and a wide range of techniques have been proposed.⁴ Nevertheless, especially in the case of solid electrodes, the measurement often remains problematic although from the available range of techniques, the study of the differential capacity minimum in dilute electrolyte solution has been the most productive of the techniques for determining the pzc of polycrystalline electrodes. However, this method is limited to the use of dilute solutions and requires the absence of specific adsorption.^{1,4} Its application to group VII metals (Pt, Pd, Rh, Ir) is therefore restricted since the pseudocapacity due to hydrogen and anion adsorption dominates the electrochemical response of the metal.²

Other techniques for the determination of pzc's rely on the direct measurement of the charge on the electrode surface. This may be achieved by recording the current transient appearing during the disappearance or formation⁵ of the electric double layer. By adsorbing CO to satiate the electrode surface, the charge of the double layer is effectively quenched. This has been used to determine the pzc of polycrystalline platinum and single-crystal electrodes.^{6–8} The removal of the electrode charge can also be facilitated by a scraping method,⁹ while laser ablation of electrode surfaces has been applied to molybdenum electrodes.¹⁰ Clearly, however, the latter two methodologies are inappropriate for single crystal electrodes. We have recently proposed a more general method for single crystals using a temperature jump applied via the sudden heating of an electrode via a nanosecond pulse from a Nd: YAG laser. By studying the current transients resulting from the thermal perturbation a correlation was observed in the sign of the double layer charge⁵ which was seen to invert on passing through the pzc.

Techniques based from observations indirectly related to the state of charge on the electrode surface include measurements

of surface stress,¹¹ the electro-capillary properties of the electrode,^{12–17} the use of dropping electrolyte electrodes,¹⁸ studies of the vibrational properties of water molecules in the interface,^{19,20} piezoelectric detection,^{21,22} mass titration,²³ the electrochemical quartz crystal balance method,²⁴ EMF measurements,²⁵ and methods based on the reduction of N₂O.²⁶

The effect of ultrasound in voltammetric experiments is now well documented and understood. First and foremost, very significantly increased mass transport can arise from the effects of acoustic streaming and from interfacial cavitation phenomena.^{30,31} The former is a nonlinear effect, which allows high-intensity sound energy to be converted in the kinetic energy of turbulent convective flow.^{30,32} Second, the cavitation can also lead to electrode depassivation through the removal of surface-active species; this has been most widely exploited in sono-electroanalysis where, for example, measurements in the presence of surfactants become quantitatively viable, in contrast to the observed voltammetric invisibility or near-invisibility under silent conditions. Both mass transport and surface activation effects have been beneficially exploited in sonoelectroanalysis. Third, sonolysis of solutions may lead to radical species, such as hydrogen atoms or hydroxyl radicals in aqueous solution, and these may become involved as chemical intermediates in electrode processes. Fourth, the emulsifying power of ultrasound enables the dispersion of heterogeneous liquid–liquid systems via “acoustic emulsification”;³³ this has been utilized in both sonoelectroanalytical work^{34,35} and, more particularly, in sonoelectrosynthesis.³³

In contrast, the effects of insonation on the properties of the electrical double layer formed at the surface of an electrode have been relatively neglected and are limited to essentially empirical exploratory studies of the possible effects of ultrasound on electrode potentials.^{27,28}

In a previous paper we have used ultrafast (“nanosecond”) electrochemical equipments and arrays of microelectrodes to investigate the nature of interfacial cavitation.²⁹ By studying the reduction of the ferricyanide anion in aqueous solution using either chronoamperometry or cyclic voltammetry it was possible to monitor the bubble activity in real time to determine bubble sizes and to gain an insight into the bubble dynamics; the latter

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suggested that microjetting was unlikely under "normal" sono-electrochemical conditions at frequencies near 20 kHz.

Using "nanosecond" voltammetry we have previously reported²⁹ that for a solution containing no electroactive species no cavitation spikes were observed under potentiostatic conditions in contrast to what was seen when a potential scan was applied. The interpretation is that no double layer charging peak is observed at constant potentials because sonication cannot remove the double layer, since the electrostatic attraction between the electrode surface and the ions of opposite charge in solution is too strong. Quantitative estimates were presented.²⁹ In contrast, if the potential varies, the charge on the electrode changes, and ions from the solution are needed to compensate the extra charge. When a bubble partially blocks the surface, double layer charging is prevented and hence a depletion in the current is observed. Upon bubble collapse, the charge is recovered over a short time, giving a sharp current peak.

In the present note, we report nanosecond chronoamperometric measurements made under variable potentiostatic conditions in a two-phase system (containing mostly water) of an aqueous electro-inactive electrolyte and heptane under acoustic emulsification. Significant current spikes are seen, attributed to the impacting of heptane droplets on the electrode surface, and found to change polarity as the electrode potential varies through the accepted potential of zero charge of the electrode material in the pertinent aqueous medium. A possible explanation is given to this observation, which suggests a new generic approach to the measurement of pzc's.

Experimental Section

Reagents. Chemical reagents used were KCl (Riedel-de Haën, analytical reagent), heptane (+99% HPLC Grade, Aldrich), decane (+99% HPLC Grade, Aldrich), HNO₃ (BDH, AnalaR), HCl (BDH, AnalaR), and HClO₄ (Aldrich, 70% ACS). These were of the highest grade available and were used without further purification. Dilute acid and electrolyte solutions were prepared using UHQ grade water of resistivity of not less than 18 M Ω cm (Elga, High Wycombe, Bucks, UK).

Instrumentation. Monitoring chronoamperometric signals for cavitation or related activity in aqueous solution is beyond the capabilities of any currently available commercial potentiostat as the cavitation activity can occur over a time scale as small as 200 ns. Accordingly, the potentiostat used was built in-house and has a scan rate of 2.5×10^6 V s⁻¹ and was used with a gain of 8.2×10^3 Ω and minimum filtering. This potentiostat is essentially that described and utilized by Amatore and co-workers.^{36,37} The potential was applied with a TTI TG1304 programmable function generator (Thurlby Thandar Instruments Ltd, Huntingdon, Cambs, UK) and the current recorded with a Tektronix TDS 3032 oscilloscope (300 MHz band-pass, 2.5 GS/s).

Microelectrodes. Pt and Au micro-disk working electrodes of 100 μ m radius (99.95%, Johnson Matthey plc, London UK) were made by sealing into soft glass according to a published procedure.³⁸ Experiments were conducted in a small volume cell (ca. 25 mL) with a conventional three-electrode arrangement within a Faraday cage. The working electrodes were polished between runs using alumina lapping compounds (BDH) of decreasing size from 25 μ m down to 0.25 μ m on glass and soft lapping pads (Kemet Ltd, UK). The polished electrodes were cleaned with ultrapure water and then immersed in approximately 30% nitric acid and stored under ultrapure water between each use. Both electrodes were electrochemically cleaned by potential cycling in the reaction solution prior to each experiment.

For measurements on gold electrodes, the reference electrode used was a Pd wire (Advent, Oxon, UK) charged with H₂ in a separate compartment.⁵ For measurements on platinum electrodes, a platinum black reference electrode was prepared according to a published procedure³⁹ and immersed in 1.18 M HCl with constant bubbling of H₂ (BOC, high purity) at 1 atm pressure. The cell containing the hydrogen electrode was connected to the reaction cell via a salt bridge containing saturated KCl solution. The counter electrode was a coiled smooth, bright platinum wire. Thermostating of the cell was achieved by the use of a cooling coil to temperatures of 22 ± 2 °C) throughout.

Ultrasonic Equipment. A 20 kHz ultrasound horn transducer system (Sonics & Materials, VCX400) with a stepped 3 mm micro tip (titanium alloy, Jencons, Leyton Buzzard, UK) was employed. The ultrasonic power was determined calorimetrically according to the procedure of Margulis et al;⁴⁰ an intensity of "15%" was found to correspond to 310 W cm⁻². The horn probe was used in a face-on geometry^{41,42} to the working electrode and positioned at a constant distance of 5 mm.

Particle Size Measurement. A commercial static light scattering instrument (Malvern Mastersizer, Malvern Instruments, Worcs., UK) was employed to measure heptane droplet size distributions.

Results

First, we investigated the system of 0.1 M perchloric acid solution using a polycrystalline gold disk electrode of radius 100 μ m. Following the mechanical and electrochemical cleaning described above, a cyclic voltammogram was recorded in pure 0.1 M perchloric acid at a scan rate of 50 mV s⁻¹. This showed features expected⁵ in voltammograms for polycrystalline gold in perchloric acid, most noticeably the maximum generally ascribed to weak adsorption of perchlorate anions.⁵

Heptane (40% v/v) was then added to the perchloric acid solution and sonicated to fully emulsify the mixture before recordings were taken. Particle size measurements indicated a mean droplet size of ca. 3 μ m. All electrical equipment was switched on for a minimum of 10 s prior to commencing recording to avoid signals due to circuit pulses and the chosen potential was set.

Significant current spikes were observed at the set potential. These were found to have durations of less than 10 μ s with a sub-microsecond rise-time. The potential was then changed and further recordings made. At each potential chosen in the range -1.00 V to +1.00 V (vs Pd/H₂), these sharp current spikes were recorded. We have estimated that the number of droplet impacts per second lies in the range of 10³ to 10⁴. The polarity of the spikes was seen to change as the potential varied through the above range, as shown in Figure 1. The transient spikes show a negative current (i.e., flow of electrons away from the electrode) at potentials negative of the transition potential, and a positive current (i.e., flow of electrons into the electrode) at potentials positive of the transition potential.

The transition potential for the switch in polarity occurred at $+0.01 \text{ V} \pm 0.01 \text{ V}$ (vs Pd/H₂), and this was found on repeat experiments to be consistent. On changing the identity of the alkane used in the emulsion from heptane to decane, the transition potential also remained at the same value. At the end of each experiment, another cyclic voltammogram was measured of the working electrode to see if there had been any observable changes in the electrode surface. It was found that the pre- and post-experiment cyclic voltammograms were visually identical.

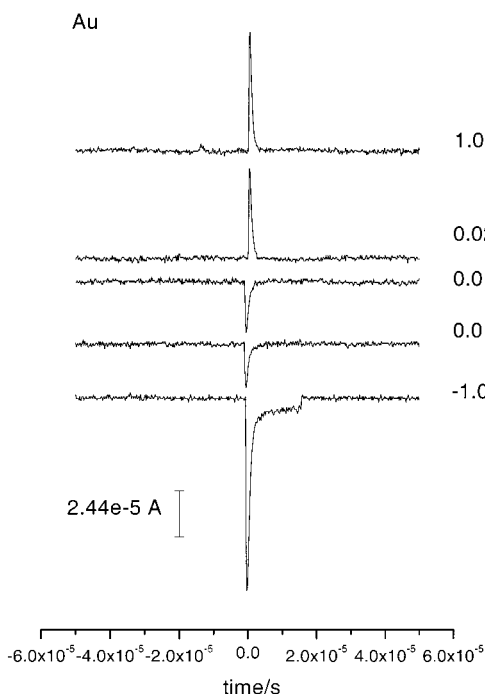


Figure 1. Current transients recorded on polycrystalline Au electrode immersed in 0.1 M HClO₄ with 40% heptane added and acoustically emulsified. The polarity of the transients inverts at +0.02 V (vs Pd/H₂).

This potential of the Pd/H₂ reference was measured to be -0.10 V (vs SCE) under the reaction conditions and found to be stable over the duration of the experiment. The transition potential of $+0.01$ V (vs Pd/H₂) can therefore be restated as equivalent to -0.09 V (vs SCE) or, by converting the SCE potential to the reference of the SHE, $+0.15$ V (vs SHE). This value coincides with reported measurements of the pzc of polycrystalline gold in the same aqueous electrolyte of $+0.10$ V and $+0.14$ V (vs SHE) using various different methods.^{4,19}

Second, we investigated the system of 0.1 M potassium chloride and 0.01 M hydrochloric acid solution with the addition of 40%(v/v) heptane using a polycrystalline platinum disk electrode of radius 100 μm . Again, after mechanical and electrochemical cleaning, a cyclic voltammogram was recorded at a scan rate of 50 mV s⁻¹; this was in good agreement with published voltammograms of this material in hydrochloric acid.⁴³

Next, the mixture of aqueous potassium chloride, hydrochloric acid, and heptane was acoustically emulsified. As with the gold electrode, significant current spikes were observed at each chosen potential. The shape and duration of the spikes were similar to those reported above, at each potential chosen in the range -1.00 V to $+1.00$ V (vs NHE). The polarity of the spikes was again seen to change as the potential varied through the above range, as shown in Figure 2. The transition potential for the switch in polarity occurred at $+0.07$ V \pm 0.01 V (vs NHE), and this was found on repeat experiments to be consistent. Furthermore, on again varying the identity of the alkane used in the emulsion from heptane to decane, the transition potential remained unchanged.

This transition potential of $+0.07$ V \pm 0.01 V coincides with the reported values of the potential of zero total charge of polycrystalline platinum in the same aqueous electrolyte of $+0.08$ V vs NHE³ and the potential of zero free charge of $+0.05$ V vs NHE³ for the same system.

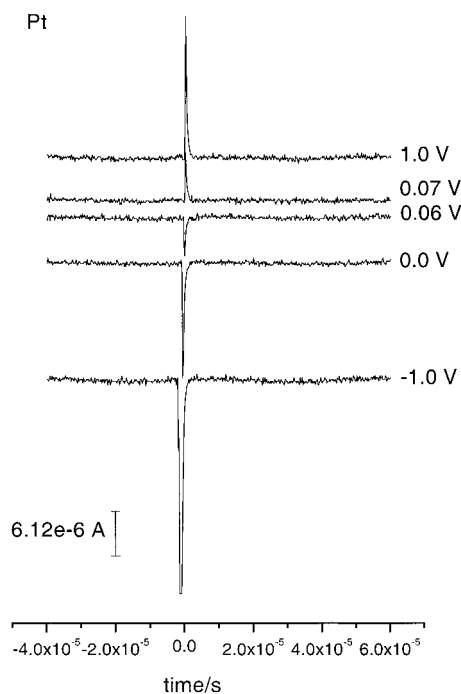


Figure 2. Current transients recorded on polycrystalline Pt electrode immersed in 0.1 M KCl, 0.01 M HCl with 40% heptane added and acoustically emulsified. The polarity of the transients inverts at $+0.07$ V (vs NHE).

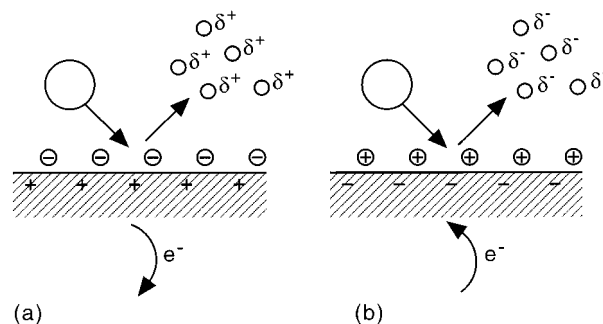


Figure 3. Schematic diagram of the process postulated to occur during droplet impact where: (a) electrode is positive of the pzc, where impact gives an "oxidative" current transient, and (b) electrode is negative of the pzc, where impact gives a "reductive" current transient.

Discussion

The results reported above empirically show an excellent correlation between the pzc of the pertinent electrode/electrolyte system and the potential at which the current transient polarity inversion occurs. At potentials positive of this point the current spikes resulting from the impinging droplets on the electrode corresponds to an "oxidation" current; electrons enter the electrode. At potentials negative of the pzc, the converse is true: electrons leave the electrode. In both cases, charges in the range 10^{-10} – 10^{-12} Coulombs are "injected" during the transient, the precise value ranging from impact to impact. In both limits the current flow is uni-directional at all measurable times implying that charge neutrality is achieved by means of a counter electrode process.

While the interpretation of these data is necessarily at present somewhat speculative, Figure 3 shows an image depicting a possible mechanism. The droplet impacting on the electrode has dimensions of a few microns, which is considerably smaller than the size of the electrode (radius 100 μm). It is therefore likely that most of the electrode/electrolyte interface is unper-

turbed by the impact. Consistent with this, the total charge carried on the electrode is likely to be in the range $20 \mu\text{C cm}^{-2}$ to $40 \mu\text{C cm}^{-2}$ corresponding for a $100 \mu\text{m}$ electrode to charges of $6 \times 10^{-9} \text{ C}$ to $1.2 \times 10^{-8} \text{ C}$, significantly in excess of those recorded. Figure 3 shows the droplet becoming charged on impact with the metallic electrode, leaving, and the direction of current flow observed. Given the magnitude of charge transferred it is likely that the droplet then fragments into tiny charged droplets to maximize the surface area containing the charge.

Conclusions

The microsecond time scale current spikes resulting from the impact of liquid alkane droplets on a potentiostated electrode in the absence of any electroactive species showed a polarity which inverts at the potential of zero charge so providing a novel and generic approach to the determination of pzc's.

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