Hydrogen evolution and oxygen reduction at a titanium sonotrode

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A titanium sonotrode is used to demonstrate that ultrasonic irradiation significantly enhances the rate of electrochemical oxygen reduction and hydrogen evolution reactions in neutral aqueous electrolyte.

The effect of ultrasound in the 15–40 kHz frequency range on the kinetics and mechanism of electrochemical reactions is a topic of rapidly growing interest. Power ultrasound produces cavitation in solution which may influence electrode processes through four distinct modes of interaction: (*i*) mass transport enhancement owing to turbulence and microstreaming,[1–4] (*ii*) continuous activation of the electrode surface,[5] (*iii*) the formation of ions, radicals and other high energy intermediates,[1] (*iv*) the mediation of chemical processes associated with heterogeneous electron transfer steps[6] and (*v*) product desorption.[7] Ultrasound baths or probes may be used to irradiate electrodes indirectly.[8] However, recent studies have demonstrated greater rate enhancement using directly stimulated 'sonotrodes' in which the solution contacting end of a ultrasonic transducer horn acts as the electrode surface.[9,10] In the work described here a titanium sonotrode was used to investigate the effect of ultrasound on electrochemical hydrogen evolution [reaction (1)] and oxygen reduction [reaction (2)] in aqueous electrolyte.

$$2H^{+}_{(aq)} + 2e^{-} \longrightarrow H_{2(g)} \qquad (1)$$

$$O_{2(aq)} + 2H_2O + 4e^{-} \longrightarrow 4OH^{-}_{(aq)} \qquad (2)$$

Reactions (1) and (2) are the cathodic reactions most commonly associated with metallic corrosion in aqueous systems and acceleration of corrosion rates in the presence of cavitation is a significant technological problem.[11] Both reactions have complex multistep mechanisms involving chemisorbed intermediates,[12,13] and reaction rates could potentially be influenced through any one of modes (*i*)–(*v*) above. In the current study we aim to determine the extent to which the cathodic processes associated with metallic corrosion are influenced by the presence of intense cavitation.

The titanium (Ti) tip sonotrode and sono-electrochemical cell arrangement, used in this work is illustrated in Fig. 1. A 20 kHz ultrasound generator (Branson Ultrasonics Sonifier 250) was used with a standard flat 10 mm titanium tip. The ultrasonic power level used throughout was 26 W cm^{-2}, as determined using calorimetry.[4] The circulation of water from a thermostated bath through a stainless steel cooling coil,[9] allowed the electrolyte temperature to be kept constant to within 1 °C during all experiments. All voltammetric measurements were carried out at 30 °C using a Solartron 1280 potentiostat under computer control. The electrolyte used was a 0.7 mol dm^{-3} aqueous Na_2SO_4 adjusted to pH 7 using 0.1 M NaOH. All chemicals were obtained from BDH at Analar grade purity and doubly distilled water was used throughout. Prior to measurement under deaerated conditions the electrolyte was purged with prepurified argon (BOC) for 30 min. Linear sweep voltammograms were recorded by sweeping the sonotrode potential from -2.5 to 0 V *vs.* SCE at 0.014 V s^{-1}. Prior to recording voltammetric data the sonotrode potential was cycled between -2.5 and 0 V at ±0.014 V s^{-1} in the absence of ultrasound until the voltammogram became reproducible ($<$ three cycles).

The voltammetric response of the Ti sonotrode in deaerated and aerated electrolyte is shown as a series of Tafel plots in Fig. 2(*a*) and (*b*) respectively; H_2 evolution occurred visibly at potentials < -1.6 V. It may be seen from Fig. 2 that the characteristic shapes of the Tafel plots remained similar under silent and sonicated conditions but that current density values were higher at all potentials in the presence of ultrasound. The magnitude of the sono-electrochemical effect, its reproducibility and reversible nature are highlighted in Fig. 3(*a*) and (*b*) for the deaerated and aerated solutions, respectively which illustrates the transient (time dependent) current responses of the sonotrode when subject to short (1–5 s) pulses of sonication at constant potential. Fig. 3(*a*) shows the response at -1.3 V in deaerated electrolyte and Fig. 3(*b*) shows the response at -1.25 V in aerated electrolyte. In both cases it can be seen that the

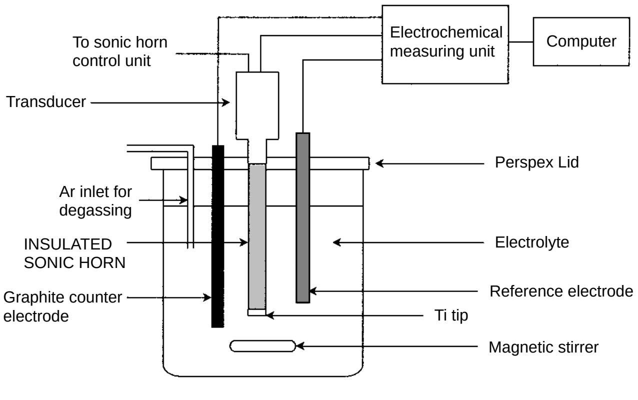

Fig. 1 Schematic diagram of sonotrode and electrochemical cell arrangement

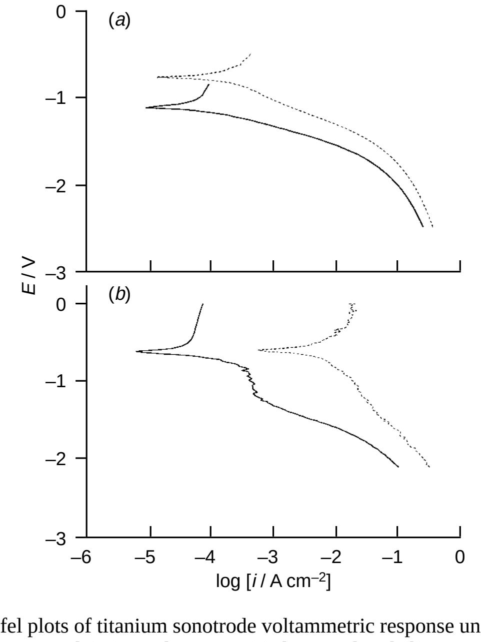

Fig. 2 Tafel plots of titanium sonotrode voltammetric response under silent (—) and sonicated (---) conditions in (*a*) deaerated and (*b*) aerated neutral 0.7 M aqueous Na_2SO_4 at 30 °C. Potential sweep rate = 0.014 V s^{-1}.

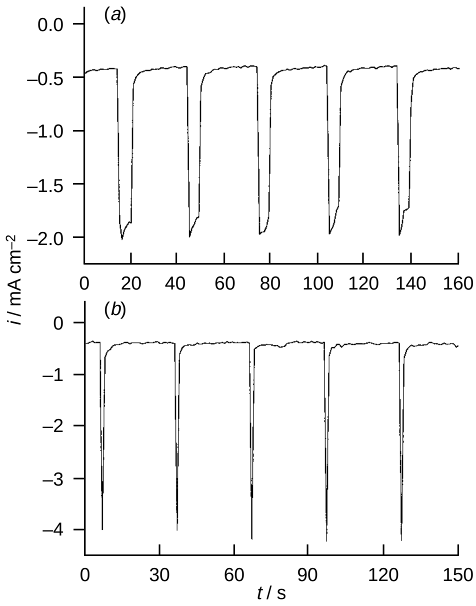

Fig. 3 Transient (time dependent) current response of titanium sonotrode in neutral 0.7 M aqueous Na_2SO_4 at 30 °C. (*a*) Deaerated, 5 s ultrasound pulses at −1.3 V *vs.* SCE. (*b*) Aerated, 1 s ultrasound pulses at −1.25 V *vs.* SCE.

changes in current density resulting from sonication are instantaneous and reversible. This finding rules out the possibility that bulk heating by ultrasound contributes significantly to the observed current density increases. The n-type semiconducting TiO_2/Ti_2O_3 layer, which rapidly forms on Ti exposed to air, can limit the rate of electrochemical reactions (especially anodic reactions) at Ti sonotrodes.[9] However, Figs. 2 and 3 suggest that the Ti sonotrode is an adequate cathode for reactions (1) and (2) at the potentials indicated and that reaction rates are significantly enhanced by sonication.

Considering the deaerated case first, it is assumed that the cathodic currents in Fig. 2(*a*) are entirely due to reaction (1). Under silent conditions the Tafel plot is approximately linear over the range −1.25 to −1.6 V which is consistent with reaction (1) being activation controlled; the Tafel slope is 190 mV decade^{-1}. At potentials cathodic of −1.7 V the Tafel plots curve in a manner suggestive of current limiting. Under sonicated conditions the Tafel plot is shifted anodically by approximately 500 mV and the Tafel slope in the linear region increases to 280 mV decade^{-1}. The change in Tafel slope is consistent with ultrasound producing a change in mechanism or rate determining step for reaction (1). Ultrasonic current density enhancement at constant potential is greatest in the linear, activation controlled region (a factor of *ca.* five) and smaller in the current limiting region (a factor of *ca.* two). Since the effect of ultrasound is greatest when reaction (1) is activation controlled it is probable that interaction with the electrochemical process occurs primarily through modes (*ii*)–(*v*) above.

Considering the aerated case, under silent conditions the Tafel plot in Fig. 2(*b*) shows a well developed current plateau between −0.9 and −1.4 V due to reaction (2) becoming limited by mass transport of O_2 to the sonotrode surface.[15] It is therefore assumed that the cathodic currents in Fig. 2(*b*) result predominantly from reaction (2) at potentials cathodic of −1.4 V, and from a combination of reactions (1) and (2) at potentials anodic of −1.4 V. Ultrasonic current density enhancement at constant potential is greatest (more than one order of magnitude) at potentials anodic of −1.4 V and the diffusion limited current plateau becomes indistinct in the sonicated Tafel plot. The current density increase between −0.9 and −1.4 V must arise primarily through mode (*i*) above and implies a decrease of at least tenfold in the effective thickness of the Nernst diffusion layer under sonicated conditions. Modes (*ii*)–(*v*) may be significant at potentials anodic of −0.9 V where reaction (2) is not mass transport limited, but mode (*i*) probably remains an important contribution to the current increase observed on sonication.

These preliminary results show that the rates of electrochemical O_2 reduction and H_2 evolution at a titanium surface are significantly increased by power ultrasound. Ultrasonically enhanced mass transport appears to be the principle cause of rate increase in the case of O_2 reduction but significant rate increase also occurs in the case of activation controlled H_2 evolution. The acceleration of both these cathodic processes may contribute to the increased rates of metallic corrosion observed in the presence of intense cavitation. Furthermore, the finding that activation overpotentials for H_2 evolution may be reduced by ultrasound suggests that electrocatalytic sonotrodes might usefully be investigated as a means of increasing the efficiency of technologically important gas evolving electrolyses.

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Notes and References

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