

# Sono-electrosynthesis: electrode depassivation and trapping of insoluble redox products

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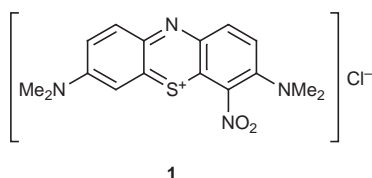
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The electrosynthesis of water-insoluble products such as *leuco*-Methylene Green from soluble precursors can be accomplished using an emulsion formed *via* insonation so that the organic phase constantly extracts the product and simultaneously prevents the electrode passivation which would occur in aqueous solution alone.

The introduction of power ultrasound into electrochemical systems has many benefits,<sup>1,2</sup> including first, extremely enhanced mass transport resulting from acoustic streaming<sup>3</sup> or microjetting,<sup>4</sup> and second, electrode activation arising from cavitation erosion.<sup>5</sup> In addition sonication has been used to permit the electrochemical study of essentially water-insoluble organic species in aqueous solution.<sup>6,7</sup>

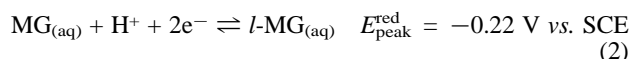
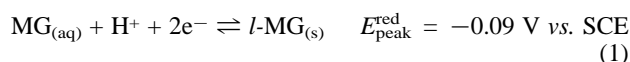
Here we report a new and general use of ultrasonically generated emulsions in electrosynthesis. Many potentially viable electrode processes are inhibited if not entirely passivated by the adsorption, precipitation or polymerisation of reaction products or intermediates on the electrode surface. This note addresses two such reactions in aqueous solution, first the two-electron reduction of Methylene Green<sup>8–10</sup> (MG, **1**) to *leuco*-Methylene Green, and second the oxidation of iodide to solid iodine,<sup>11–13</sup> both at platinum electrodes.



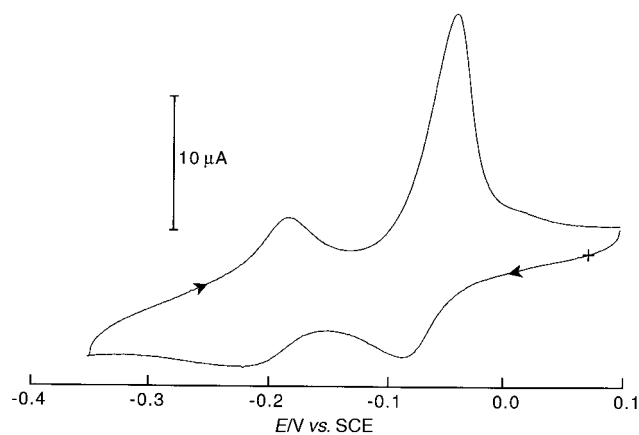
The presence of an organic phase which emulsifies under insonation is shown to lead to (i) 'clean' useful voltammetry, (ii) the extraction of reduction products and (iii) the preservation of electrode activity where in aqueous solution alone passivation would preclude useful electrosynthesis.

Experiments were conducted using a 250 ml sonovoltammetric cell at 20 °C, which incorporated a 13 mm diameter, 20 kHz titanium tipped ultrasonic horn probe (Sonics & Materials). Ultrasound power levels up to 50 W cm<sup>-2</sup> were employed<sup>14,15</sup> and electrochemical measurements carried out using a commercial three-electrode potentiostat (Eco-Chemie, Utrecht) except that the horn probe was electrically isolated as previously reported.<sup>16</sup> Full descriptions of sonoelectrochemical and sonovoltammetric procedures have appeared elsewhere.<sup>17</sup>

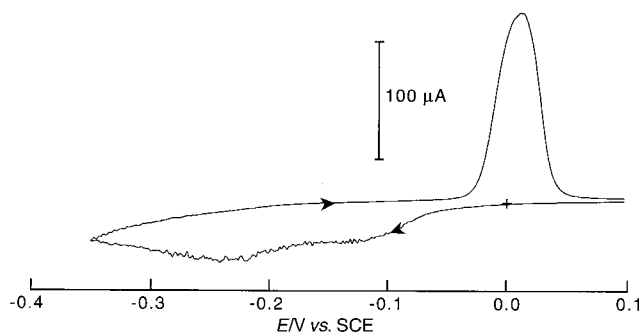
Cyclic voltammograms for 0.2 and 2 mM aqueous solutions of Methylene Green in 0.1 M KCl, buffered at pH 6.5 ± 0.1 with 0.2 M KH<sub>2</sub>PO<sub>4</sub>, were recorded in quiescent solution. A typical 'silent' voltammogram is shown in Fig. 1. The two peaks can be attributed to the processes in eqn. (1) and (2), where *l*-MG is *leuco*-Methylene Green. The two-electron character of each wave was evidenced first by Tafel analysis and second by the observation that the reduction potentials shifted by ca. 30 mV per pH unit in the pH range 6 to 8 consistent with a two-electron, one proton reduction. Notice the large 'stripping' peak corresponding to the re-oxidation of the insoluble surface-bound *leuco*-Methylene Green.



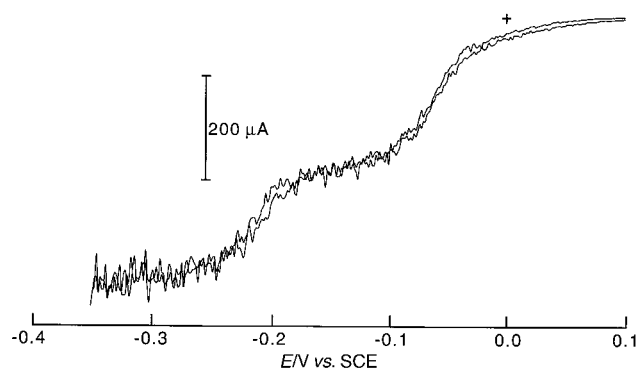
When 25 W cm<sup>-2</sup> of power ultrasound is introduced into the cell the voltammetry changes markedly due to the significantly enhanced mass transport and is shown in Fig. 2. Notice first that a much larger stripping peak is seen corresponding to the greater deposition resulting from the enhanced currents flowing due to the increased mass transport. Second, whilst there is a mass-transport limited current analogous to a polarogram relating to the two-electron processes, reflecting the constant flux of material due to steady-state convection/diffusion, the wave at the more negative potential shows a progressive decrease of signal at potentials negative of ca. -0.23 V vs. SCE. This electrode passivation was also seen (i) under silent conditions and (ii) during hydrodynamic voltammetry (for example at a channel electrode) and effectively precludes the electro-



**Fig. 1** 'Silent' cyclic voltammogram of 0.2 mM MG in 0.1 M KCl/0.2 M KH<sub>2</sub>PO<sub>4(aq)</sub> at pH 6.5. Scan rate was 10 mV s<sup>-1</sup> and the working electrode was a 6 mm diameter Pt disc.



**Fig. 2** Cyclic voltammogram of 0.2 mM MG in 0.1 M KCl/0.2 M KH<sub>2</sub>PO<sub>4(aq)</sub> at pH 6.5. 25 W cm<sup>-2</sup> ultrasound was employed at a horn-to-electrode distance of 22 mm. Scan rate was 10 mV s<sup>-1</sup> and the working electrode was a 6 mm diameter Pt disc.



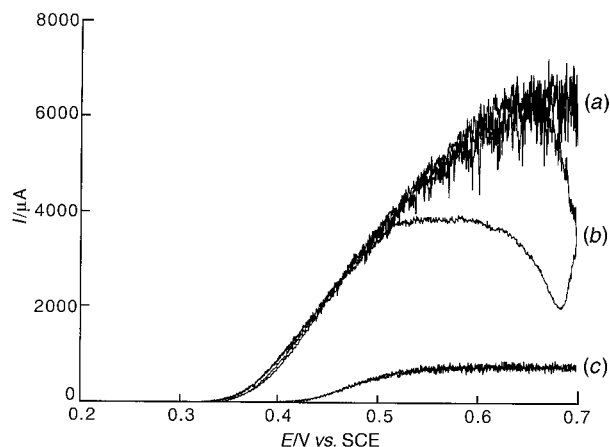
**Fig. 3** Cyclic voltammogram of 2 mM MG in 0.1 M KCl/0.2 M  $\text{KH}_2\text{PO}_4(\text{aq})$  at pH 6.5 and 20% (v/v) toluene (emulsified).  $18 \text{ W cm}^{-2}$  ultrasound was employed at a horn-to-electrode distance of 19 mm. Scan rate was  $10 \text{ mV s}^{-1}$  and the working electrode was a 6 mm diameter Pt disc.

synthetic generation of useful quantities of *leuco*-Methylene Green. However when voltammetry is conducted using a 20% (v/v) solution of toluene in water and  $18 \text{ W cm}^{-2}$  ultrasound is utilised to form an emulsion, the sonovoltammetry is very different, as shown in Fig. 3. Now, two steady-state sigmoidal reduction waves are observed with no evidence of a stripping peak on sweeps to positive potentials. Similar effects were seen using *n*-octane instead of toluene. We attribute this to the solubility of the reduction product in the emulsified organic phase that bathes the electrode surface. This was confirmed using a 30 min sono-electrolysis experiment during which the potential of the solution (200 ml of 2 mM MG in 0.1 M KCl/0.2 M  $\text{KH}_2\text{PO}_4$  at pH 6.5 and 50 ml of toluene) was maintained at  $-0.35 \text{ V vs. SCE}$  under ultrasound. The toluene reaction mixture was then isolated under argon, evaporated to dryness and the product dissolved in octane for UV-visible characterisation of the *leuco* base via the peak at 263 nm.<sup>18</sup>

Examination of Fig. 3 shows two roughly equal waves corresponding to the two electron reduction of Methylene Green giving respectively solid *l*-MG and aqueous phase *l*-MG. The former, of course, is rapidly removed by the emulsion. The relative sizes of the two waves reflect the amount of material that can nucleate and adsorb in the case of the first wave and the fact that the overall magnitude of the two waves taken together reflects the rate of mass transport of MG to the electrode surface. The scope for 'clean' voltammetric measurements in otherwise passivating systems in the presence of ultrasound is evident.

The oxidation of iodide at platinum electrodes is complicated by the formation of solid iodine at higher concentrations when the solubility of iodine is exceeded (1.1 mM in water at 25 °C).<sup>19</sup> Cyclic voltammetry of 1 and 10 mM aqueous solutions of KI in 0.125 M  $\text{H}_2\text{SO}_4$  was performed under  $19 \text{ W cm}^{-2}$  ultrasound at a horn to electrode distance of 12 mm. This is shown in Fig. 4. At the higher concentration the voltammetry deviates from the expected steady-state behaviour and heavy electrode passivation leads to current fall-off. When 10% (25 ml) of the aqueous solution was replaced with  $\text{CH}_2\text{Cl}_2$  and the mixture was emulsified, steady-state behaviour was achieved and is seen in Fig. 4(c). This was confirmed spectroscopically to be due to the dissolution of iodine from the platinum electrode.

Sonication is a convenient and effective alternative to the use of high-speed stirring and/or detergents for the promotion of emulsions for electrochemistry,<sup>20</sup> although the possibility of a small amount of parallel chemistry resulting from sono-decomposition of the solvents (water, toluene and dichloromethane) should be noted.



**Fig. 4** Cyclic voltammograms on a 6 mm Pt disc electrode at  $10 \text{ mV s}^{-1}$  for (a) 1 mM and (b) 10 mM KI in 0.125 M  $\text{H}_2\text{SO}_4$ .  $18 \text{ W cm}^{-2}$  ultrasound was employed at a horn-to-electrode distance of 12 mm. Trace (c) is as for (b) except that 10% (v/v) of the aqueous solution was replaced with  $\text{CH}_2\text{Cl}_2$  and emulsified.

The use of the sono-emulsion technique to depassivate electrochemical systems promises much for synthetic, mechanistic and analytical studies and can be expected to considerably broaden the range of chemical systems amenable to electrochemical study.

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## Notes and references

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