

SONOELECTROCHEMISTRY - AN EMERGING AREA

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Ultrasonic (US) radiation in liquid media is known to produce chemical effects with significant acceleration of reaction rates. Influence of US on electrochemical processes—sonochemistry—is not totally new. Extensive studies have been reported on the relaxation phenomena and structure of electrolyte solutions, with the help of ultrasounds. However, investigations on the influence of ultrasound on electrode reactions and electrosyntheses are of recent origin. Ultrasonic radiation, known to produce cavitation and microstreaming phenomena in liquid media, has resulted in very high current densities and a modified pattern of product yields during electrochemical reactions. Thus, interfacing ultrasound with electrochemistry appears to hold a lot of potential and the field of sonochemistry is set to make new strides. Recent investigations in this area carried out in our laboratories and elsewhere are reviewed in this communication.

INTRODUCTION

Sonochemistry, the chemical effects of intense sound waves travelling through a liquid, have been known since 1927. However, a renaissance in sonochemistry took place in the 1980's, when inexpensive and reliable generators of high intensity ultrasound (US) became commercially available.

The interaction of sound with liquids results in a phenomenon called cavitation which is capable of generating very high temperatures and pressures, thus making available a range of energies on time and space scales that are not normally available from other sources [1,2]. The advantage of using US in synthetic organic chemistry has been well described [3]. US is reported to promote cyclo-addition [4] and asymmetric syntheses [5]. The progress in the field of sonochemistry over the last one or two decades can be gauged from the fact that an international symposium on sonochemistry was organised by the Royal Society of Chemistry in 1986.

Sonochemistry of a solid surface present inside a liquid assumes a special significance since when cavitation occurs in a liquid in contact with a solid surface, the cavity implosion is no longer symmetrical and spherical as observed in liquid-only systems. Consequently, the implosion being markedly asymmetric, leads to rapid movement of fluids and microstreaming [6] at the solid-liquid interface. This factor provides great impetus for bringing in US influence on electrochemical reactions. Thus the emergence of sonochemistry adds one more important dimension to electrochemistry. In this report, a brief review of the potentialities of US for electrochemistry with possible future scenarios is presented.

The use of US as an auxiliary tool in electrochemical processes is well established over the years. Extensive work has been reported [7] based on studies with high frequency US. In these investigations, the effect of the medium under investigation upon the US waves has been studied. Variation of velocity and absorption coefficient of US waves as a result of interaction with the medium have been studied and such studies have been employed for the elucidation of the structure of electrolytes and their complexes in solution.

US waves have also been used for bringing about intensive stirring and agitation of the electrolyte during cleaning and electroplating operations. Agitation of the bath with US waves is found to increase the hardness and reduce the porosity of copper electrodeposits [8].

Very recently, the effect of US on metal powders was studied and the results [9] show that the activity of nickel and copper

metal powders is enhanced enormously. Particle surfaces are smoothened, surface oxide coating is removed and catalytic activity of Ni powder for alkene hydrogenation increases by about five orders. Inter-particle collisions driven by the turbulent flow caused by US irradiation is attributed to be the reason for the enormous increase in activity. The crystal orientation of copper electrodeposit from an acidic sulphate bath is found to be influenced by the US agitation; surface activation potential for the electrodeposition is reported to be increased by 50 fold in the presence of US waves [11]. The foregoing results clearly indicate that in heterogeneous situations, like in electrochemical reactions, the presence of US waves can bring about significant changes.

In the electrochemical oxidation of cyclohexane carboxylate, US favours the dominance of two-electron products together with increased reaction efficiency as against an equal preponderance of both one-electron and two-electron pathways under normal conditions [12]. US radiation is found to promote organic synthesis [4,5,13]. US has been shown to provide a versatile method for carrying out heterogeneous reductions [14]. The passage of US through a liquid medium is reported to modify the normal molecular translational motion which may influence vibrational and rotational energy levels [15]. Polythiophene films prepared by electrochemical oxidation showed superior characteristics if the oxidation was done in the presence of US [16]. Electroless nickel plating in the presence of US irradiation, results in harder deposits whose microstructure is altered [17]. US induced electrochemical synthesis is claimed to be an elegant method for preparing organo-transition metal chalcogenides [18]. The above results indicate that US-mediated reactions are becoming important in synthetic schemes. Many such reaction mechanisms are not yet fully understood; however, cavitation and metal surface scrubbing are attributed to be largely responsible for the observed effects, especially more so in situations involving solid-liquid interfaces [6].

The behaviour of the model redox system viz. ferrocyanide-ferricyanide in the presence of US radiation has been investigated here. An ultrasonic bath [RETSCH, Type USG; 35 kHz] was used for generating ultrasound. The cell had a typical three electrode configuration with a platinum wire as working electrode, a platinum foil as counter electrode and a standard calomel electrode as reference electrode. The cell containing ferrocyanide and ferricyanide of 1 mM concentration each in 0.5 M KCl was dipped into water taken in the ultrasonic bath. A Potentiostat (POS 73, Wenking) along with an x-y recorder (Rikadenki RT-201) was employed for recording the voltammograms. The resulting voltammograms are given in Fig. 1. In the presence of US

irradiation, the voltammograms have an oscillatory behaviour; **smoothed** out curves are given in the figure.

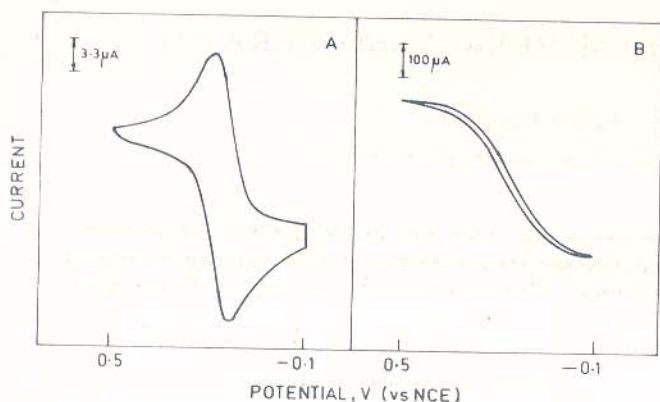


Fig. 1: Voltammogram for the ferrocyanide/ferricyanide (1mM each) in 0.5M KCl on Pt at a sweep rate of $20 \text{ mV}\cdot\text{s}^{-1}$ (A) in the absence of US and (B) in the presence of US

It can be seen that in the presence of US, (i) the magnitude of the current is very high—about 20 times larger than that obtained in the absence of US, (ii) the voltammograms appear sigmoidal, resembling the behaviour encountered with microelectrodes, (iii) the magnitude of the current in the presence of US, is independent of sweep rate, unlike under normal conditions where increase in sweep rate enhances the current (iv) With background electrolyte alone, the voltammogram is not at all influenced by the US irradiation, (v) as the concentration of the redox species is increased, the setting in of the limiting region in the sigmoidal behaviour of the voltammogram in presence of US is delayed.

These results clearly show that in the presence of US, the magnitude of current is large and this may largely be attributed to the increased mass transfer. This enhanced mass transport resulting in larger magnitudes of current will push down the detection limits in analytical applications. It is relevant here to note that indeed such an effort has been parallelly made resulting in the development of ultrasonic hydrodynamic modulation voltammetry [19]. Cavitation bubbles at or near the electrode surface can be expected to raise the limiting currents attainable as a result of a reduction in diffusion layer thickness.

At this juncture, it is interesting to see whether US can bring about any effect other than enhancing the mass transport. The following observations show that US has a great role to play: (i) presence of US alters the product distribution pattern during electrooxidation [12] (ii) electropolymerisation of polythiophene in presence of US results in higher electrical conductivity of the film [16] and (iii) structure and properties of electrodeposits are altered in the presence of US [8,10,17]. Further, US is reported to alter the surface morphology of Cu and Ni metal powders significantly and enhance their catalytic activity by about five orders for alkene hydrogenation [9]. Very recently it has been reported

[15] that the passage of US through a liquid medium modifies the normal molecular translational motion and that depending on the efficiency of the acoustic relaxation mechanism, some of the increased translational energy may be converted to vibrational and rotational energies. Recent studies [20] on sonochemical reactions seem to indicate that sonication promotes reactions proceeding through radical pathways. The foregoing observations suggest that US can influence the chemistry of reactions besides mass transport. In electrochemical reactions, processes such as ionic solvation and adsorption/desorption on electrode surfaces are bound to be influenced by the US waves. Accordingly, detailed and systematic investigations are needed in the following directions: (i) role of frequency of US waves on electrochemical reactions (analogous to the influence of frequency in impedance spectroscopy), (ii) influence of US waves through solvent reorganisation, which according to Marcus theory is a prerequisite for electron transfer reactions, (iii) effect of US on mass transfer (diffusion and forced convection). It will also be of interest to establish a correlation between the frequency and intensity of US with convectioal velocity generated. The field of sonoelectrochemistry is in its infancy and its many interesting facets need to be unravelled.

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