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In Situ Monitoring of Electrochromic Systems by Peizoelectric Detector Photoacoustic Spectroscopy of Electrodes

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The in situ detection of surface changes of electrodes and measurement of the absorption spectra of surface films was carried out by photoacoustic spectroscopy utilizing a piezoelectric ceramic detector attached to the back of a metal foil electrode. The technique was applied to two electrochromic processes involving heptyl viologen dibromide and WO_3. Absorption spectra for both systems were obtained together with the results of simultaneous cyclic voltammetry and photoacoustic spectroscopy. The coloration response times of both systems were also measured.

Photoacoustic spectroscopy (PAS) has recently been the subject of much interest as a technique especially suited to the measurement of absorption spectra of solids in contact with gases, see, e.g., (*1, 2*) and references therein. Typically the sample is placed in a sealed, gas-filled, cell of fixed volume, containing a sensitive microphone as a detector and irradiated with high intensity, chopped monochromatic light. The light absorbed by the sample is converted to heat by radiationless processes giving rise to pressure changes within the cell, which can be detected with the microphone and processed further. While PAS microphone techniques have been useful for studies of solids in contact with gases, they have not been readily applied to solid–liquid interfaces, such as the electrode–solution interface. Recent innovations in this technique have involved the use of piezoelectric ceramics in place of a microphone both in the measurement of absorption spectra of liquids (*3*) and solids in contact with gases (*4*). In the latter case (*4*), a piezoelectric ceramic was attached to a front surface mirror, the sample was placed on the front of the mirror, and the thermally generated elastic waves (*5*) resulting from the absorption of electromagnetic radiation by the sample were detected. With this arrangement, the acoustic impedance mismatch across the interface between detector and sample was apparently minimized, resulting in a much larger transmission coefficient for the acoustic wave and thus a much larger signal compared to the conventional PAS cell (*4*).

We recently reported preliminary experiments using piezoelectric detector techniques to monitor solids in contact with liquids (*6*). We describe here electrochemical applications of this technique. By attaching a piezoelectric ceramic to the back of a metal foil electrode, it is possible to detect the presence of colored surface films on the electrode and measure photoacoustically their absorption spectra. We demonstrate the technique for two systems: the reduction of heptyl viologen dibromide and tungsten trioxide; both of these have been the subject of much recent interest because of their electrochromic properties and their potential use as display devices (*7–12*).

EXPERIMENTAL

A one-compartment cell was used with a Pt wire counter electrode and a saturated calomel reference electrode (SCE). The working electrode (Figure 1) was constructed by attaching a piezoelectric ceramic disk (Edo Western Corp., Salt Lake City, Utah) to either 0.05-mm Pt or 0.025-mm W foil with epoxy cement (Devcon, 5-min). Lead C contacted the Pt working electrode which was controlled by the potentiostat in the usual electrochemical three-electrode cell arrangement. The leads to the conductors plated on both sides of the piezoelectric disk (D) were connected to the preamplifier of the lock-in amplifier. Care was taken to ensure that the foil electrode was electrically insulated from the piezoelectric disk and the disk from the solution by the epoxy cement.

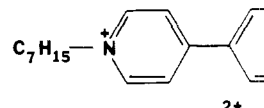
The photoacoustic spectrometer, consisting of a 2500-W xenon arc lamp, a PAR 192 variable frequency chopper (Princeton Applied Research Corp.) and a Jarrell-Ash 82-410 Monochromator, has been discussed in detail previously (*13*). The signal from the piezoelectric disk was synchronously detected at the chopper frequency (15 or 96 Hz) with a PAR 5204 lock-in amplifier and recorded on a Bascom-Turner 8110 data processing and storage recorder.

Electrochemical measurements were carried out with a PAR 173 Potentiostat together with a PAR 175 Universal programmer and the cyclic voltammograms recorded on a Houston Instruments 2500 X-Y recorder. All potentials are reported against SCE.

RESULTS AND DISCUSSION

Background Behavior. The piezoelectric signal (PS) spectrum obtained from the clean Pt electrode in H_2O is shown in Figure 2. Both this spectrum and that obtained from the clean W electrode, which was similar to Figure 2, were essentially the same as the power spectrum of the lamp (as measured with a radiometer) (*13*). All spectra were corrected for the spectral distribution of the lamp-monochromator by dividing the signal intensity at a given wavelength by that of the clean electrode at the same wavelength. All of the piezoelectric signals reported are averages of more than one set of data which have been smoothed and normalized. The results are thus presented in arbitrary units.

Heptyl Viologen on Pt. To test the applicability of the piezoelectric detection technique to the determination of the absorption spectra of films deposited on an electrode surface, the reduction of heptyl viologen (HV^{2+}) bromide was investigated. Reduction of this species leads to the formation of



HV^{2+}

a film of the deeply colored salt, HVBr, on the electrode surface. The cyclic voltammogram of a 10^{-2} M solution of HV^{2+} in 0.3 M KBr at the Pt piezoelectric electrode is shown in Figure 3. The cathodic wave at −0.53 V corresponds to the one-electron reduction of HV^{2+} (*8*):

$$HV^{2+} + Br^- + e \rightleftarrows HVBr$$

and was accompanied by the characteristic deep purple coloration of the viologen cation radical precipitate on the electrode surface. Reoxidation of this layer at −0.48 V on the return scan again produced a clean electrode surface. The piezoelectric spectrum of the HVBr layer recorded while maintaining the electrode potential at −0.6 V is shown in Figure 4. There is good agreement between this spectrum and the reported absorption spectrum of a thin HVBr layer on SnO_2 glass measured spectrophotometrically (*14*). When

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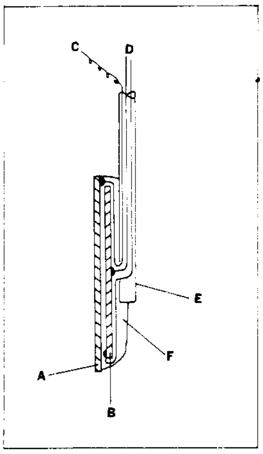

Figure 1. The working electrode. (A) Pt or W foil, area ~2 cm^2; (B) piezoelectric ceramic; (C) lead to potentiostat; (D) leads to lock-in amplifier; (E) Pyrex glass tube; (F) epoxy cement

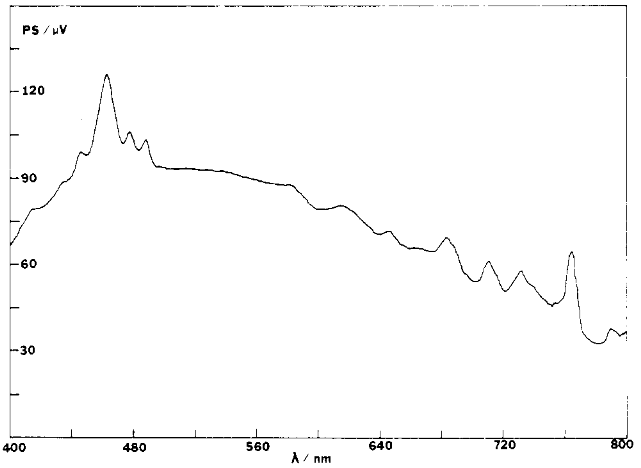

Figure 2. Piezoelectric signal (PS) spectrum of the Pt electrode. Experimental conditions: 10-nm resolution; 100 nm s^{-1} scan rate; 0.3 s lock-in amplifier time constant. Average of 2 scans

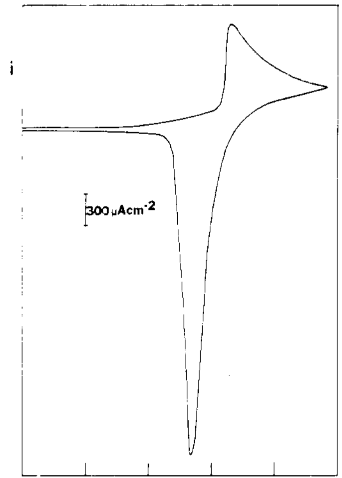

Figure 3. Cyclic voltammogram of 10^{-2} M heptyl viologen dibromide in 0.3 M KBr at the platinum electrode. The potential was swept at 20 mV s^{-1} from -0.2 to -0.7 V vs. SCE and back

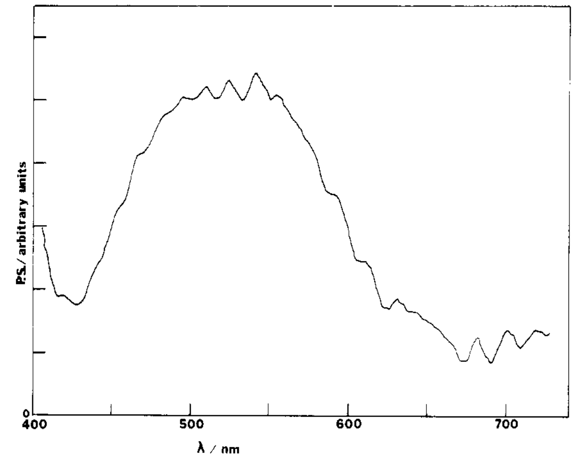

Figure 4. Piezoelectric spectrum of deposited film of HVBr on the Pt electrode. Experimental conditions are the same as in Figure 2. Average of 4 scans

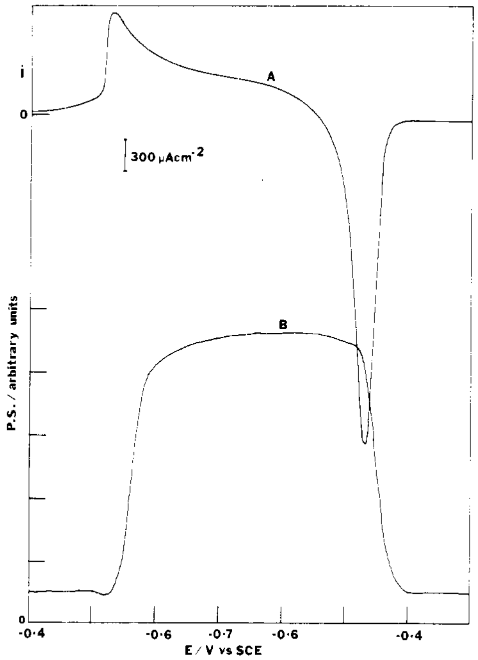

Figure 5. Simultaneous recording of current (A) and piezoelectric signal (PS) (B) for the deposition and stripping of HVBr at a Pt electrode as the potential was scanned from -0.3 to -0.7 V vs. SCE and back at 20 mV s^{-1}. λ = 550 nm. Average of 2 scans

the piezoelectric response was monitored at a wavelength of 550 nm, corresponding to the absorption maximum in Figure 4, cycling the potential between -0.4 and -0.7 V (Figure 5A) gave rise to the change in piezoelectric signal shown in Figure 5B. The number of coulombs corresponding to the cathodic (coloration) and anodic (bleaching) steps were equal. The increase and decrease in the signal essentially coincided with the reduction and oxidation waves of the cyclic voltammogram. Moreover, after a coloration and bleaching cycle, the signal returned to the precoloration level, demonstrating complete removal of the film from the electrode surface. The piezoelectric signal level at saturation represents the formation of several hundred monolayers of the HVBr precipitate (based on ~2.5 μC/cm^2 for the production of a monolayer). The coloration response time of the system to a potential step is also of importance in electrochromic display devices. The piezoelectric signal response at 550 nm on stepping the potential from -0.2 to -0.6 V is shown in Figure 6. The potential step was initiated at the time indicated by the arrow. The minimum which occurs immediately following the potential step probably represents the direct effect of surface tension changes at the electrode–solution interface which is detected by the piezoelectric detector, as discussed previously (*15*). The signal increased to a constant value in about 0.8 s with a response time to 90% of maximum coloration of ~0.5 s for this electrode system.

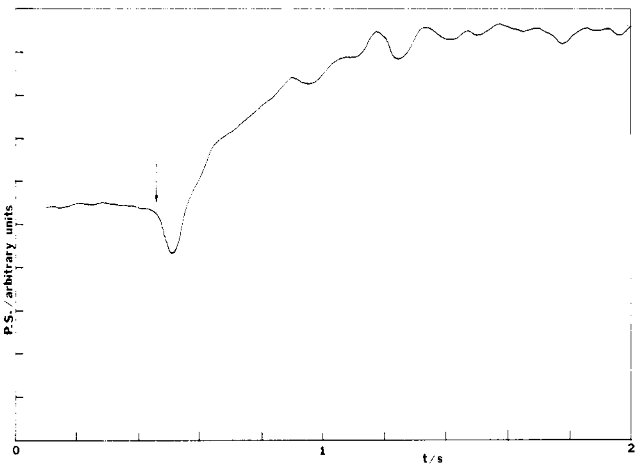

Figure 6. Piezoelectric signal (PS) response of the Pt electrode in 10^{-2} M HV^{2+}–0.3 M KBr solution at λ = 550 nm on stepping the potential from −0.2 to −0.6 V. Lock-in amplifier time constant, 1 ms

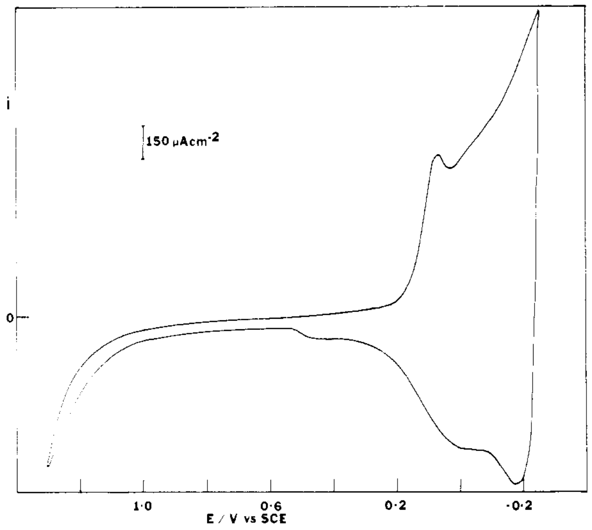

Figure 7. Cyclic voltammogram of a ~300-Å thick WO_3 film on the W electrode in 1 M H_2SO_4. Scan rate: 200 mV s^{-1}

Anodic WO_3 on W. Another system which has been investigated for possible application to electrochromic display devices involves the coloration of WO_3 on reduction and its bleaching on subsequent oxidation. A WO_3 film ~300 Å thick was grown on the W piezoelectric electrode by repeated cycling between +1.3 and −0.25 V in 1 M H_2SO_4 for ~2 h (*10*). The cyclic voltammogram after this time is shown in Figure 7. The anodic current commencing at ~ +0.2 V is attributed to the formation of the hydrogen tungsten bronze (*10–12*):

$$WO_3 + xH^+ + zH_2O + xe^- \rightleftarrows H_x(H_2O)_zWO_3$$

which results in a blue coloration of the oxide film. Scan reversal at −0.2 V produced an anodic current due to bleaching of the reduced layer back to its original pale yellow color. The piezoelectric spectrum of the WO_3 layer in its bleached (A) and colored (B) forms is given in Figure 8. The signal increase at ~380 nm for both forms corresponds to the band gap of amorphous WO_3 and is in agreement with the reported absorption spectrum for WO_3 on SnO_2 glass (*12*). The principal absorption peak for colored WO_3 is centered at 900 nm (*12*), beyond the range of the Xe lamp–monochromator system used here. However the edge of this peak extends to the absorption at 380 nm and this is the cause of the difference observed in Figure 8 between the bleached and colored forms. The dependence of the coloration and bleaching processes on potential was investigated by scanning the electrode potential from +0.5 to −0.25 V and back while simultaneously monitoring the cyclic voltammetric current (A) and the piezoelectric signal (B) with irradiation at 550 nm. The results are shown in Figure 9. As with the HV^{2+} system, coincidence was observed between the current (A) and the increase and decrease in piezoelectric signal (B) which corresponded to coloring and bleaching of the film. Note that for the anodic WO_3 films the bleaching commenced immediately after reversal of the direction of the voltage scan as predicted previously from the cyclic voltammetric behavior (*10*). The response time for coloration of the film was determined by stepping the potential from +0.5 to −0.25 V and monitoring the piezoelectric signal. The results shown in Figure 10 indicate a response time of ~0.8 s which is in good agreement with that determined by previous *i–t* measurements (*10*).

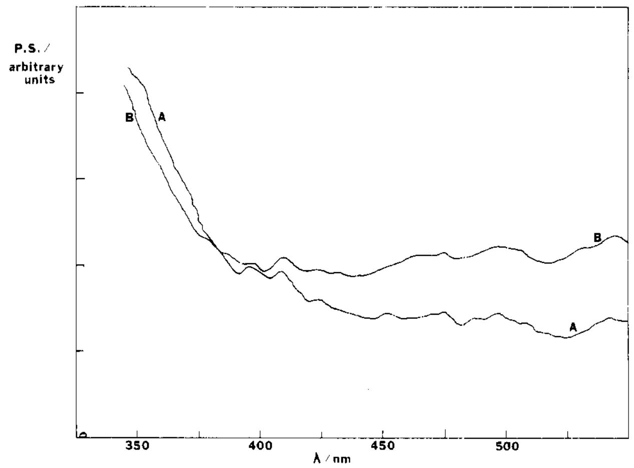

Figure 8. Piezoelectric signal (PS) spectra of the WO_3 film on the W electrode (A) at +0.5 V (bleached) and (B) at −0.25 V (colored). Experimental conditions as in Figure 2. Average of 4 scans

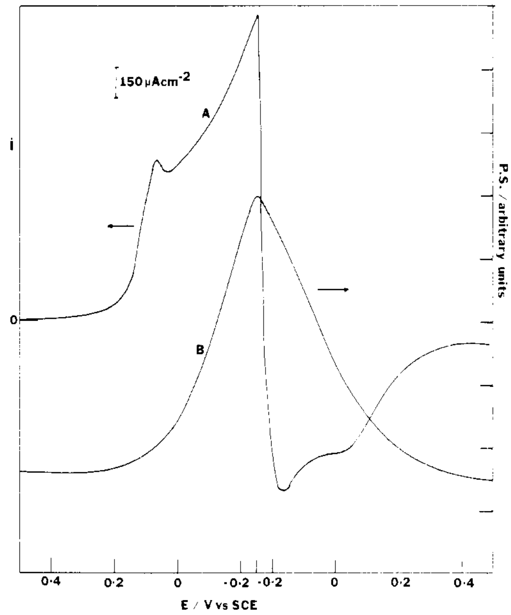

Figure 9. Simultaneous recording of current (A) and piezoelectric signal (PS) (B) for WO_3 on the W electrode with the potential scanned from 0.5 to −0.2 V and back at a scan rate of 50 mV s^{-1}. λ = 500 nm. Average of 2 scans

CONCLUSIONS

The results presented here show that this technique offers an easy alternative to conventional spectroelectrochemical methods (*16, 17*). Because reflected or transmitted light is not detected by this technique, it is applicable to a wide variety of electrode materials (e.g., opaque or sintered powder materials) making it especially useful for the in situ study of new

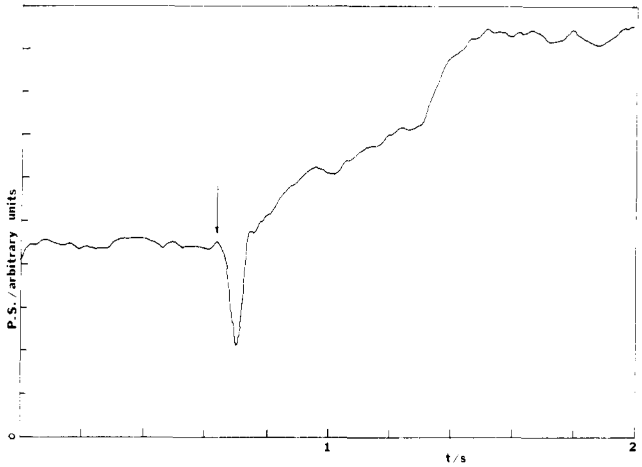

Figure 10. Piezoelectric signal (PS) response of the WO_3 layer on the W electrode at $\lambda = 550$ nm on stepping the potential from +0.5 to −0.25 V. Lock-in amplifier time constant, 10 ms

electrochromic systems. The technique could also be applied to changes in the solution layer near an electrode surface by monitoring decreases in the piezoelectric signal on the electrochemical formation of a colored species which absorbs the impinging radiation. Although a few preliminary experimental studies of this sort have been carried out, this application does not seem to have significant advantages over more conventional spectroelectrochemical techniques. Finally this is, to our knowledge, the first application of PAS techniques to the in situ study of electrochemical systems. Experiments in progress (*18*) utilizing pulsed excitation of the electrode–piezoelectric transducer system with a dye laser suggest that the sensitivity of the technique can be improved to allow monolayer detection of highly colored layers (e.g., HVBr) with ~μs response times.

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Simultaneous Elimination of Sodium-24, Potassium-42, Bromium-82, and Phosphorus-32 in the Determination of Trace Elements in Biological Materials by Neutron Activation Analysis

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A group separation for the determination of trace elements in dry biological material is described. In comparison with sophisticated automatic systems, this method is simple, reliable, and applicable in every radiochemical laboratory. After irradiation in a thermal-neutron flux of 5×10^{12} cm^{-2} s^{-1}, the samples are mineralized in 1:1 H_2SO_4/HNO_3, using a Teflon-lined pressure decomposition vessel. The trace elements of interest are concentrated on active carbon by performing a few successive filtrations, after addition of a suitable combination of reagents and adjusting the pH in each step. The main interfering radionuclides ^{24}Na, ^{42}K, ^{82}Br, and ^{32}P are eliminated very efficiently during this concentration step. One sample of ~100 mg is reduced to two or three counting aliquots only, in which some 25 elements are determined. The chemical procedure is completed with a purely instrumental determination of some major and minor elements. Results obtained for reference materials from NBS and IAEA are given.

Instrumental neutron activation analysis of biological material is seriously hampered by the interfering radionuclides ^{24}Na, ^{32}P, ^{42}K, ^{38}Cl, and ^{82}Br. Chemical separations are usually based on some combination of distillation and ion-exchange (*1–4*). Alternatively, use is made of inorganic adsorbents (*5*, *6*). The first approach is rather time-consuming, while the second may cause serious losses.

In view of the successful application of active carbon in the concentration of trace elements from water samples (*7–10*), it was felt that a rapid and reliable method of elemental analysis could be obtained by applying the following sequence:

Irradiation–wet mineralization–adsorption on active carbon–γ-spectrometry.

Irradiation of up to 40 samples packed in polythene capsules is performed for 12 h in a rotating facility at $\phi_{th} = 2 \times 10^{12}$ cm^{-2} s^{-1}.

After 12 hours cooling, mineralization with H_2SO_4/HNO_3 takes place in a Teflon-lined pressure vessel. After dilution with water, the distillate is filtered to collect any undissolved silica. Then the pH is adjusted and chelating agents are added. The solution is led through a 50-mg layer of active

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