

## Gravimetric Electrochemical Voltage Spectroscopy: *In Situ* Mass Measurements during Electrochemical Doping of the Conducting Polymer Polypyrrole

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(Received 16 August 1984)

A new technique is described for direct measurement of mass changes of a conducting polymer electrode during electrochemical cycling. A quartz microbalance is used, with one of its contacts serving as the working electrode. Its high sensitivity permits resolution of mass changes less than 100 ng/cm<sup>2</sup>. The results demonstrate that on reduction of poly(pyrrole perchlorate), charge compensation is achieved by diffusion of the lithium cation into the polymer and not the perchlorate anion into solution.

PACS numbers: 06.60.-c, 07.10.+i, 82.45.+z

In this Letter, we report the development of a new electrochemical technique, gravimetric electrochemical voltage spectroscopy (GEVS), which employs a quartz resonator to determine the mass changes associated with incremental changes in dopant concentration measured by the EVS<sup>1-3</sup> method. The quartz resonator is used as the substrate for the working electrode in an electrochemical cell. This highly sensitive device is used in conjunction with electrochemical voltage spectroscopy to measure the change in mass of a polypyrrole film during electrochemical reduction and oxidation. Since the oscillator is only sensitive to reactions that involve weight changes at the working electrode (e.g., doping and undoping the polymer), one can distinguish electrochemical currents which are associated with such mass changes from those which are not.

As demonstrated by Nomura and Minemura,<sup>4</sup> a quartz resonator will oscillate in solution provided that only one side of the crystal is exposed to the conducting electrolyte/solvent. When one face of the crystal is immersed in solution, the resonant frequency decreases from the free-air value ( $f_0$ ). Kanazawa<sup>5</sup> demonstrated that the change in frequency upon immersion is given by

$$\Delta f = - (f_0^3 \rho_L \eta_L / \pi \rho_Q \mu_Q)^{1/2}, \quad (1)$$

where  $\rho_L, \eta_L$  are the density and absolute viscosity of the liquid, and  $\rho_Q, \mu_Q$  are the density and shear modulus of the quartz. This decrease in resonant frequency [typically about 800 Hz for a 5-MHz crystal in tetrahydrofuran (THF)] is due to the fact that the shear wave penetrates the solvent about 1000 Å before being damped out. Since the wave is exponentially damped in solution,<sup>5</sup> the crystal senses about 500 Å of solvent. There is an additional contribution to the frequency shift resulting from surface roughness in which the solvent is carried along in pockets on the surface.<sup>6</sup> The magnitude of this

effect depends on the solvent density and roughness of the crystal. For our oscillators, in THF, this amounts to about 1000 Hz.

Since the polymer thickness is small compared to the thickness of the crystal, the shear wave is not significantly damped and we may treat the polymer as a rigid film. The resonator then senses the entire mass of the polymer as well as a constant contribution due to the penetration of the shear wave into the solvent, and the effects of surface roughness. If the mass of the polymer increases (e.g., through electrochemical doping), the resonant frequency will decrease by an amount<sup>7</sup>

$$\Delta f = - [2f_0^2 / (\rho_Q \mu_Q)^{1/2}] \Delta M / A, \quad (2)$$

where  $A$  is the area of the resonating quartz and  $\Delta M$  is the increase in mass due to the incorporation of dopant ions (and solvent molecules) into the structure of the polymer. Constant-current growth measurements show the linear relationship in Eq. (2) to be obeyed for film thickness well above those used in the following studies. Therefore, the rigid-film approximation above is valid.

In order to expose only one face of the resonator to the solvent, an electrochemical cell (Fig. 1) was designed with a 5-MHz *AT*-cut quartz resonator (Valpey-Fisher) sealed to the bottom of a  $\frac{1}{2}$ -in.-i.d. Pyrex tube with 5-min epoxy. The crystal was  $\frac{1}{2}$  in. diam  $\times$  0.33 mm thick with chrome-gold "keyway" contacts on each face. The epoxy seal was cured in a 60°C oven for at least 24 h. The inside of the tube was then treated with a 50/50 sulfuric acid/hydrogen peroxide (30%) solution to oxidize any organics present. The cell was then rinsed with distilled water, acetonitrile, and THF, and redried in an oven before being moved to a controlled-atmosphere dry box. A 4000-Å film of polypyrrole was then grown on the inner gold contact of the cell by use of a platinum counter electrode and 0.1-M pyrrole + 0.1-M AgClO<sub>4</sub>/acetonitrile solution.<sup>8</sup> Af-

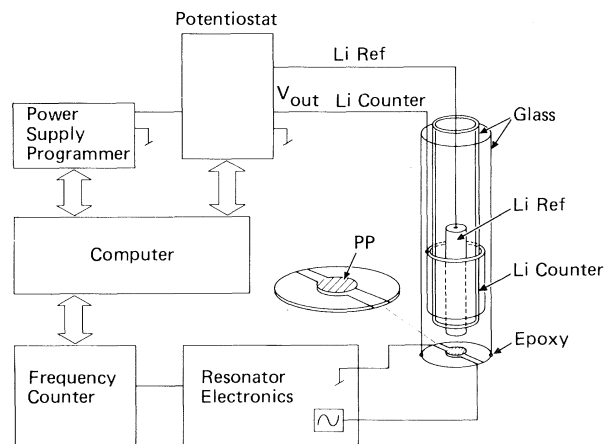


FIG. 1. The GEVS apparatus.

ter polymerization, the platinum counter electrode was removed and the cell washed in pure acetonitrile and allowed to dry thoroughly. A solution of 1-M  $\text{LiClO}_4/\text{THF}$  was then added to the cell along with the lithium counter and reference electrodes. Prior to use the  $\text{LiClO}_4$  was melted under dynamic vacuum and the THF was vacuum distilled from potassium benzophenone and passed through a column of activated alumina in a drybox.

The GEVS technique consists of a potentiostat, power supply programmer, and frequency counter (see Fig. 1) interfaced to a computer. The experiment begins after the electrochemical cell is allowed to equilibrate at some initial voltage ( $V_{\text{init}}$ ). The cell is then displaced from equilibrium by a potential step  $\Delta V$  (0.02 V). Current flows through the cell, decaying as the polymer dopes or undopes and the working electrode comes to equilibrium at the voltage  $V_{\text{init}} + \Delta V$ . The cell current is integrated during the voltage step, and when the current falls below a designated minimum value ( $0.1 \mu\text{A}$ ), the integration is stopped. This cutoff current is kept small to insure quasiequilibrium. The integrated current yields the charge  $\Delta Q$  that flowed during the voltage step  $\Delta V$ . The resonant frequency of the crystal is also measured at the end of the step and the differential charge, voltage, and frequency are stored on a magnetic disk. The voltage is then stepped an additional  $\Delta V$  and the process repeated until some extremum voltage is reached. The sign of  $\Delta V$  is then reversed and the voltage stepped back to the initial value. The procedure is repeated for a number of cycles. The derivative  $dV/dQ$  can later be integrated to obtain the voltage-versus-charge relation for the cell. The frequency-voltage relation determines the mass-voltage relation for the cell [see Eq. (2)]. Alternatively, it is possible to plot

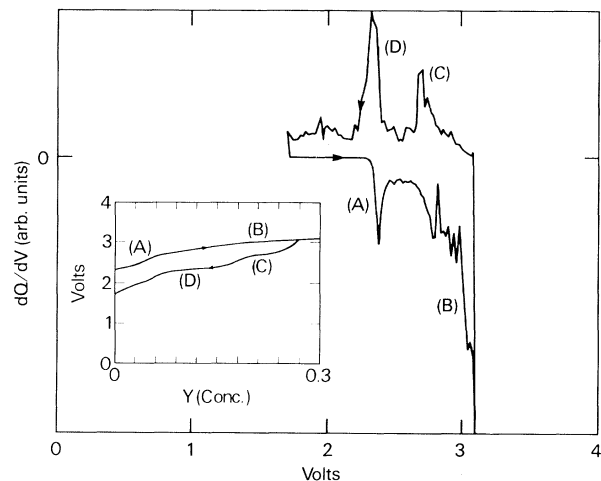


FIG. 2. The GEVS data  $dQ/dV$  vs  $V$  (inset shows  $V$  vs  $Q$ ). Oxidation occurs at peaks A and B while reduction occurs at C and D.

the derivatives  $dQ/dV$  and  $-df/dV$  ( $\propto dM/dV$ ) as a function of applied voltage.

Figures 2 and 3 show the derivatives  $dQ/dV$  and  $-df/dV$  versus voltage, respectively. The insets show  $V$  vs  $y$  and  $V$  vs  $f$  where  $y$  is the dopant concentration (in mole percent) per pyrrole unit. The figures may be treated as infinitely slow cyclic voltammograms in that they represent the differential charge (or mass) transferred as a function of voltage (vs Li). Oxidation peak A in Fig. 2 fixes the threshold for hole injection (oxidation) at  $2.38 \pm 0.02$  V. A secondary oxidation peak (B) occurs above 3.02 V. Two peaks are also observed upon reduction at  $2.70 \pm 0.02$  V (C) and  $2.32 \pm 0.02$  V

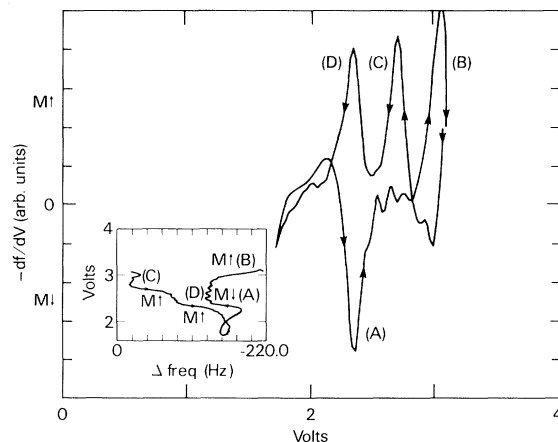


FIG. 3. The GEVS data  $-df/dV$  vs  $V$  determines the differential mass changes associated with the oxidation and reduction features in Fig. 2. The up arrow ( $\uparrow$ ) indicates increasing mass, ( $\downarrow$ ) indicates decreasing mass.

(D). Figure 3 shows corresponding mass changes at the same energies. Features B, C, and D indicate increasing mass of the polymer while feature A indicates mass loss.

The data in Fig. 3 and the absence of mass changes in background scans (i.e., no polymer on working electrode) indicate that the mass changes observed are intrinsic to the electrochemistry of polypyrrole. Furthermore, the fact that the polymer mass *increases* upon reduction suggests that injection of electrons into the material results in lithium ions diffusing into the polymer (as opposed to perchlorate diffusing out). We note that this mass increase is not a result of swelling (solvent uptake) of the undoped polymer. When the same experiment is performed with polypyrrole(toluenesulfonate), the mass decreases upon reduction and increases upon reoxidation. If polypyrrole was more heavily solvated in its neutral state (which is unlikely for a moderately polar solvent like THF), the polypyrrole(toluenesulfonate) sample would also exhibit a net mass increase on reduction. We believe that the effect is due to ion pairing of the dopant with the cation of the polymer. Small anions like  $\text{ClO}_4^-$  are known to form ion pairs with organic cations [like (polypyrrole) $^+$ ], and this may impede their mass transport. As a result charge compensation could occur via the more rapid diffusion of the  $\text{Li}^+$  cation. The data in Fig. 3 are a direct observation of this phenomenon. Certainly both species ( $\text{ClO}_4^-$  and  $\text{Li}^+$ ) may be diffusing throughout the cycle, but a net increase in mass on reduction of oxidized polypyrrole indicates a net uptake of lithium. Reoxidation of the film does not, however, involve only perchlorate diffusion. Peak A (Fig. 3) shows that initially lithium ions diffuse back out of the polymer as it is doped with perchlorate. It is only at the secondary oxidation level (B) that additional perchlorate is brought into the film. This emphasizes the inherent difference between oxidation and reduction. On reduction of a film oxidized with perchlorate, charge neutrality can be maintained *either* by outward diffusion of the anion, *or* inward diffusion of the counterion. Oxidation, on the other hand requires the presence of the anion. If insufficient perchlorate resides in the film (as  $\text{Li}^+ + \text{ClO}_4^-$  pairs) to achieve a given oxidation level, additional perchlorate *must* diffuse into the polymer. This accounts for the mass increase above 3.02 V.

As grown, polypyrrole is in the oxidized form with one perchlorate per three pyrrole units. No lithium ions are present in the synthesis. We note that the data in Figs. 2 and 3 represent the first cy-

cle for the polypyrrole electrode. The fact that the polymer exhibited a net weight increase over this cycle suggests that there exists a net concentration of lithium in both the oxidized and neutral material. After multiple cycles both the charge and mass changes become reversible over a cycle and the redox features A,B and C,D spread out in voltage. This may be understood in terms of charge localization due to increasing structural disorder induced by doping and undoping the polymer. It is interesting that for the first few cycles, the peak widths [full width at half maximum (FWHM)] of the redox features in the GEVS data are consistent with the ideal peak widths (0.09 eV) predicted for a reversible one-electron process by the Nernst equation.

The electronic band structure of conducting polymers plays an important role in their electrochemistry. As discussed elsewhere,<sup>2,3</sup> if there are no states available in the band gap of one of these (undoped) semiconductors, initial injection of unpaired charges must occur near a band edge. This accounts for the sharp oxidation threshold (2.38 V) observed in Figs. 2 and 3. The fact that doping of polypyrrole results in the formation of polaron and bipolaron states in the band gap<sup>9,10</sup> may account for the hysteresis in the  $V$  vs  $y$  relation (Fig. 2 inset) and the double reduction and oxidation levels observed in Figs. 2 and 3. The difference in energy between the oxidation levels is consistent with the difference between the polaron (0.12 eV) and bipolaron (0.69 eV) binding energies.<sup>9,10</sup> We note that similar charge-voltage features have been observed in graphite batteries and have been attributed to staging. However, since polypyrrole is highly amorphous, it seems unlikely that an intercalation effect is responsible here. The fact that oxidation at 2.38 V is associated with decreasing mass (lithium diffusing out) while oxidation above 3.02 V results in weight uptake (perchlorate diffusing in) suggests another explanation for the double oxidation levels. Some activation potential may be required to force additional perchlorate into the film.

The multiple oxidation and reduction levels observed with GEVS were not resolved by fast cyclic voltammograms (or even GEVS when the minimum current was set too high). This demonstrates the value of applying quasiequilibrium techniques in studying the electrochemistry of conducting polymers. If the dopants are not allowed to diffuse into the film, one is only sensitive to changes on the surface of the working electrode, thus sacrificing orders of magnitude sensitivity.

The quartz microbalance used in conjunction with electrochemical techniques such as EVS provides

information on the doping and undoping of conducting polymers unavailable through other techniques. It is now possible to distinguish electrochemical currents which result in mass changes from those which do not. One can in principle separate currents which are due to electrochemical doping, degradation, or side reactions. By changing the electrolyte and/or solvent, one can obtain valuable information on the composition of doped polymers in the battery configuration. The technique is highly sensitive to both dopant and solvent incorporation in the working electrode film. We have shown that for polypyrrole perchlorate versus lithium electrochemical cell, transport of  $\text{Li}^+$  ions is favored over  $\text{ClO}_4^-$ . We are now generalizing the technique to apply the resonator to the study of changes in mass as a function of time after a step in potential ("chronogravimetry"). This will allow a direct measure of the diffusion kinetics at the polymer electrode. Similar techniques have been applied to the study of polymer growth yielding valuable compositional and kinetic information.

We thank Dr. Kenneth Wynne for many useful

discussions and the Office of Naval Research for partial support of this work.

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