Estimation of Equilibrium Capacitance of Polyaniline Films Using Step Voltammetry

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The equilibrium charge storage characteristic of polyaniline films has been determined using step voltammetry technique. The step coulogram (plot of charge stored versus potential) consists of five distinct regions, which correspond to the different energy bands exhibited by the film, in keeping with Raman and ESR spectroscopy data. The coulogram is piecewise linear, with constant capacitance in each band. Effect of the type and concentration of the acid on the equilibrium capacitances of the bands has been studied. The polaron band has the highest capacitance, followed by the bipolaron band and then the polaron lattice band. The charge stored at a given potential is found to be proportional to film mass. The film needs to be polarized to a threshold charge before faradaic charging begins. This faradaic threshold is independent of the type and concentration of the acids. The step coulogram is compared with the sweep coulogram obtained from linear sweep voltammetry. At low sweep rates, the sweep coulogram also exhibits five distinct bands. However, with increase in the sweep rate, the bands progressively reduce in number. The capacitance of the polaron band decreases linearly with square root of sweep rate and attains the equilibrium capacitance at zero sweep rate.

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In this work, we have developed a technique based on step voltammetry to estimate equilibrium charge storage characteristics of conducting polymer films. This technique allows all relaxation modes of conducting polymer chains to be observed. Each of these rearrangements is associated with a corresponding relaxation time. When the film is charged under potentiodynamic conditions, only those relaxation modes, the time constants of which are comparable to the time scale of variation of the potential, are operative. Hence, for fixed values of the initial and the final potentials, the amount of charge accumulated in the film can vary widely depending on how fast the potential is varied between these values. This strong dependence on dynamics renders accurate estimation of equilibrium energy density difficult. It is not possible to use very slow rates of variations of potential due to significant interference from stray currents. Although, one may attempt to estimate equilibrium energy density by extrapolating the potentiodynamic data to zero sweep rate/frequency, the accuracy and reliability of such estimates is questionable.

In this work, we have developed a technique based on step voltammetry to estimate equilibrium charge storage characteristics of conducting polymer films. This technique allows all relaxation modes of the polymer to be operative. We have shown that the film capacitance obtained using potentiodynamic techniques, such as cyclic voltammetry, is lower than that obtained using the technique developed here. We refer to the latter as the equilibrium capacitance. It is a thermodynamic characteristic of the conducting film and hence is unique. Moreover, dependence of the equilibrium capacitance of a film on the electrode potential reveals different regimes, or energy bands of charging of the film. These bands manifest under the potentiodynamic charging process only at very low scan rates. We have demonstrated the technique using polyaniline as a model ICP. The technique is briefly described as follows.

We subject polyaniline films, grown on a rotating disk electrode, to step change in potential from initial potential of −0.2 V with respect to SCE. The choice of the initial potential is based on the fact that charge in the film at this potential is practically zero. After the step change, we allow sufficient time for the polymer film to attain the equilibrium at the imposed potential and measure the amount of charge accumulated in the film at the end of this period. We progressively increase the step size and find the charge stored at equilibrium as a function of the electrode potential. When the charge stored in the film is plotted against the electrode potential, the resulting coulogram....
exhibits five distinct linear regions (bands) with each band having a constant capacitance.

The present technique provides an accurate and reliable estimate of the energy density of a conducting polymer electrode. Although, this technique is developed using polyaniline films, it is a general technique and can be used to obtain the equilibrium charge storage characteristics of any conducting polymer.

Experimental

Both the deposition of the film and the chronoamperometry were conducted in a single compartment three electrode cell. All chemicals were analytical grade and obtained from reputable companies. The sulfuric acid used in the study was of microelectronic grade (J.T. Baker, USA). Mill-Q water was used for dilution. Aniline was distilled to a colorless product before use. A 5 mm diameter platinum rotating disk (Pine Instrument Company) was used as the working electrode. All experiments were conducted at temperature of 298 K in a 200 ml capacity, three necked flask. The counter electrode was a fine platinum mesh having 45 mm length and 10 mm width, and a saturated calomel electrode was used as the reference electrode. The potentiostat (CH Instrument, USA) used for the measurement had the potential range of ±10 V, current range of ±2 A, and the input impedance at the saturated calomel reference electrode of 1012 Ohm.

The film was deposited on the electrode by anodic electropolymerization from a solution containing 0.1 M aniline and 0.5 M sulfuric acid. Prior to deposition of the film, the platinum electrode was polished using 0.05 μm alumina paste and then activated by potential cycling between 0 V and 1 V in 0.5 M sulfuric acid for ten cycles. Polyaniline film deposition was performed in two steps. During the first, the electrode potential was cycled three times between −0.2 V and 1.0 V at the sweep rate of 50 mV/s. The electrode was rotated at 3000 rpm during this step. Subsequently, the electropolymerization was continued between −0.2 V to 0.75 V on the stationary electrode, at the same scan rate, till the peak current density of the first anodic wave, \( i_p \), reached a specific value. The electrode was kept stationary in this step. This procedure yielded highly reproducible films as shown later in the results. In this study, we have used the peak current density (\( i_p \)) of the first anodic wave of the last synthesis cycle, as the measure of the film mass. This is based on the finding of Stilwell and Park.23

During the step voltammetry experiment, the electrode was subjected to three potential steps. In the first, the potential was stepped up from the base potential (−0.2 V) to the end potential. Subsequently, it was stepped down to the base potential and finally it was stepped up again to the final step potential. After each step change, a time period of 20s was allowed for the transience to die down (except in 5 mM sulfuric acid where the transience was slow and hence 40 s of transience-time was provided). The charge accumulated in the film during the first potential step was different from the subsequent two steps, which exhibited equal absolute charge. This could be due to residual charge remaining in the film before the step voltammetry experiment commenced. Only the data obtained for the third (charging) step was used for the further analysis. Most experiments were performed in aqueous sulfuric acid. However, a few experiments were also performed in aqueous hydrochloric acid and perchloric acid.

Results and Discussion

Correcting chronoamperometric data for stray current.— A typical chronoamperogram obtained form step-voltammetry is shown in Figure 1. It is seen from the figure that the current density decays rapidly with time and attains a constant value. Most of the drop in current occurs within first 0.1s. However, a very small residual current density persists. We analyze this residual current as follows. The inset of the figure shows the plot of charge density in the film versus time up to 1000s. After the initial transient, the charge density increases linearly with time, indicating a constant magnitude of the residual current. The residual current, obtained from the slope of the straight line in the inset is 0.015% of the initial current. We emphasize that this residual current is not associated with the charging/discharging process, otherwise it would have decayed with time due to progressive decrease in the available chargeable sites. Constant value of the current is indicative of stray redox reactions occurring in the film. We can therefore exclude this current from the charging current by subtraction from the total current.

The corrected current (charging current) versus time plot was integrated in order to estimate the stored charge. This charge can be considered as equilibrium charge. It is possible that the residual current hides very slow modes of charging of the film. However, from a practical point of view, these modes are not important and could be ignored.

Step coulogram and its characteristics.— During each run, the polyaniline film was subjected to a sequence of potential steps and the equilibrium charge in the film after each step was measured. In all steps, the initial potential (base potential) was fixed at −0.2 V and the step size was sequentially increased in increments of 12 to 13 mV. A typical plot of charge density (charge per unit area of the disk) versus the end potential is shown in Figure 2. We call this plot the ‘step coulogram’.

Figure 1. Variation of the current density versus time during a step voltammetry experiment on polyaniline film (\( i_p = 35.6 \text{ A.m}^{-2} \)) in 0.5 M Sulfuric acid. Potential step: −0.2 V to +0.5 V. The inset shows charge density stored with time for a step voltammetry experiment performed over 1000 s under identical conditions.

Figure 2. Step Coullogram of polyaniline film with \( i_p = 35.6 \text{ A.m}^{-2} \) in 95.2 mM Sulfuric acid. The inset shows the average step coulogram (with error bars) of six different polyaniline films prepared under identical conditions.
The reproducibility of the coulogram was checked as follows. The inset of Figure 2 shows the mean coulogram (along with error bars) of six different films prepared using the standard protocol (described in the Experimental section) with \( i_p = 35.6 \text{ A.m}^{-2} \). The average deviation of the six coulograms from the mean coulogram is only 3.34\% indicating good reproducibility of the synthesis technique. In view of this, and also of the fact that film undergoes degradation at the high end of the potential used in the experiments, a separate film was used for determination of each step coulogram.

The step coulogram in Figure 2 exhibits five distinct linear regions, or bands. These bands are the same as those obtained from ESR and Raman spectroscopy data as shown in Figure 3. These bands are named as: 1-leucoemeraldine, 2-polaron, 3-polaron lattice, 4-bipolaron and 5-pernigraniline, in keeping with the polyaniline structure and state of delocalization of charge in these bands.\(^{24,25}\) Transition from one band to the next is smooth. We have superimposed the best-fit straight lines on each band. The film acts as linear capacitor in each band, with the capacitance of the pernigraniline band is zero since all the chargeable sites are charged at the beginning of this band. We also see that the polaron lattice band has the highest share of the stored charge (although its capacitance is lower than that of the polaron and bipolaron bands) since it spans a much wider range of potential.

To study the effect of the film mass on the charge storage, step voltammetry experiments were performed on the films with different values of \( i_p \) (peak current density of the first anodic wave of the last synthesis cycle), ranging from 18.1 A.m\(^{-2}\) to 105.4 A.m\(^{-2}\). The resulting coulograms are shown in Figure 4a. We observe that the charge stored increases with increase in the value of \( i_p \). The coulograms were normalized by dividing the charge by the corresponding values of \( i_p \). The average of the normalized coulograms is shown in Figure 4b along with the error bars. The percent deviation from the mean coulogram is only 2.74\%, indicating that the charge storage characteristics are directly proportional to \( i_p \).

That \( i_p \) is an indicator of the film mass is borne out by the previous studies of Stilwell and Park.\(^{23}\) There are other parameters associated with the film mass such as anodic charge, cathodic charge and the redox charge (charge accumulated in the first anodic wave) of the last synthesis cycle. In the inset of Figure 4b it seen that these quantities are also proportional to \( i_p \). Hence any one of these quantities can be used to normalize the film charge in constructing the normalized step coulogram.

**Effect of concentration of acid on step coulogram.**—Figure 5 shows step coulograms in five different concentrations of sulfuric acid in the range spanning 5 mM to 1 M. All coulograms reveal the band structure innate to polyaniline film. We also find that the potential range of the coulograms can be divided into two zones which are separated by a crossover potential (about 0.3 V) as indicated in the figure. Below the crossover potential, the dependence of the stored charge on the acid concentration is not monotonic. However, specific trends are observed beyond the crossover potential. They are (i) the charge in the film decreases with increase in acid concentration upto

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**Table I. Summary of energy bands of polyaniline film and their characteristics.** The step coulograms of six polyaniline films shown in the inset of Figure 2 are used for this analysis.

| Polymer structure | Potential Range, versus SCE, V | Potential Range from ESR\(^{25}\), versus SCE, V | Specific Capacitance, F/m\(^2\) | Fraction of the total charge storage % |
|-------------------|---------------------------------|-----------------------------------------------|-------------------------------|--------------------------------------|
| Leucoemeraldine   | −0.2 to 0.075                   | −0.2 to 0.05                                  | 18.6 ± 0.78                   | 6.3                                  |
| Poloron           | 0.075 to 0.19                   | 0.05 to 0.15                                  | 671 ± 8.57                    | 31.1                                 |
| Polaron Lattice   | 0.19 to 0.55                    | 0.15 to 0.50                                  | 217 ± 6.17                    | 41.5                                 |
| Bipolaron         | 0.55 to 0.675                   | 0.50 to 0.725                                 | 333 ± 9.58                    | 21.1                                 |
| Pernigraniline    | >0.675                          | >0.725                                        | 0                             | 0                                    |

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\( \text{ESR} \) and \( \text{SCE} \) taken from Ref. \(^{25}\).
500 mM sulfuric acid, beyond which it is independent of the acid concentration; (ii) the maximum charge attained by the film (in the pernigraniline region) increases with decrease in the acid concentration up to 20 mM sulfuric acid, beyond which it is independent of the acid concentration.

The capacitances of the bands in different concentrations of the acid are listed in Table II. The first observation from Table II is that the capacitance of the leucoemeraldine band is insensitive to the concentration of the acid beyond 95 mM concentration. Below this concentration, the capacitance decreases with decrease in the acid concentration. The second observation is that the capacitance of the polaron band decreases with increase in the acid concentration, passes through a minimum at around 95 mM concentration and increase again beyond this concentration of the acid. On the other hand, the capacitance of the polaron lattice and the bipolaron bands show monotonic increase with decrease in the acid strength. These observations are explained below.

The following three factors govern the equilibrium charge storage characteristics of the polyaniline film

(i) Polyaniline sites are only partially protonated in sulfuric acid. Oxidation of the protonated sites is accompanied by expulsion of protons from the film, whereas oxidation of the unprotonated sites is accompanied by insertion of anions (bisulfate ions, in the present case) into the film. It is highly likely that the unprotonated sites are present in the crystalline regions of the film which become increasingly accessible as the polymer film undergoes swelling. Swelling of the film increases with increase in the electrode potential. Hence we expect accessibility of the sites to increase as the electrode potential increases.

(ii) The film consists of fine pores. The charge on the surface of the pores is balanced by the counterions which form an electric double layer, the thickness of which is of the order of the Debye length. When Debye length is comparable to pore radius, overlapping of the double layers occurs. This results in increase in energy of the system leading to lowering of the capacitance. The Debye length increases as the inverse square root of ionic strength of the solution. Hence, we expect the capacitance to decrease with decrease in the acid concentration.

(iii) Swelling also depends on the osmotic driving force. The osmotic driving force increases with decrease in concentration of the acid. Hence the film swells more in dilute solution compared to concentrated solutions. Swelling increases the pore size as well as accessibility of chargeable sites. Increase in the pore size reduces the double layer interaction and hence increases the capacitance.

Factors (ii) and (iii) show opposite effect of the acid concentration on the film capacitance. In the region beyond the crossover potential, swelling is substantial and hence factors (i) and (iii) dominate over factor (ii) listed above. This explains the monotonic increase in the stored charge as well as specific capacitance with decrease in the acid concentration in the polaron lattice and bipolaron bands. It also explains why the highest charge attained by the film increases with decrease in the acid concentration. In 20 mM concentration of the acid, all accessible sites are charged at the end of the bipolaron band.

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**Table II. Equilibrium Capacitance (F/m²) of Energy bands observed in a polyaniline film.** The data are obtained from the Step Coulograms of polyaniline film with \( i_p = 35.6 \text{ A.m}^{-2} \).

| Acid Concentration | Leucoemeraldine | Polaron | Polaron Lattice | Bipolaron |
|--------------------|-----------------|--------|-----------------|----------|
| 1000 mM            | 14.5            | 1187   | 177             | 177      |
| 500 mM             | 16.1            | 931    | 176             | 176      |
| 95.2 mM            | 16.4            | 725    | 212             | 370      |
| 19.8 mM            | 16.1            | 937    | 272             | 512      |
| 5 mM               | 7.11            | 1273   | 366             | 579      |

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**Figure 4.** (a) Step coulograms of polyaniline films of varying thickness. The peak current of the first anodic wave of polyaniline synthesis by potentiodynamic electropolymerization varies as follows: Black squares \( i_p = 18.1 \text{ A.m}^{-2} \); Red half circles \( i_p = 35.2 \text{ A.m}^{-2} \); Blue triangles \( i_p = 69.8 \text{ A.m}^{-2} \); Green inverted triangles \( i_p = 105.4 \text{ A.m}^{-2} \). (b) shows the normalized step coulogram (with error bars) of films with different thicknesses. The inset shows a plot of film charge density as a function of peak current density for polyaniline films of different thicknesses. Black squares- anodic charge; Red circles- cathodic charge; Blue triangles- redox charge.

**Figure 5.** Step coulograms in different concentrations of sulfuric acid. Key-Black squares:1000 mM; Orange inverted triangles: 500 mM; Red circles: 95.2 mM; Blue triangles:19.8 mM; Green diamonds:5 mM.
No more chargeable sites are available when the acid concentration is decreased further. Hence, the highest attainable charge in 5 mM acid is the same as that in 20 mM acid. However, because the film has greater extent of swelling in 5 mM acid, the maximum charge is attained at a lower potential.

In the region below the crossover potential (polaron band) all three factors listed above should be taken into consideration in determining the capacitance. At very low concentration, high accessibility scores over greater double layer interaction and this results in high capacitance. On the other hand at high acid concentration, lower double layer interaction scores over accessibility and we again observe high film capacitance. Hence a minimum capacitance is observed at an intermediate acid concentration.

Effect of type of acid on step coulogram.—Figure 6 shows step coulograms of nearly the same strength of three different acids. The three step coulograms do not significantly differ from each other except in the region beyond 0.6 V. The important point to note here is that the maximum charge density attained by the film in HCl (259 C.m\(^{-2}\)) is higher than the other two acids. The maximum charge density in H\(_2\)SO\(_4\) has the lowest value (216 C.m\(^{-2}\)) with HClO\(_4\) having an intermediate value (231 C.m\(^{-2}\)). This effect is possibly associated with the size of the hydrated anions of the acids. The hydrated radii of the three anions are in the order of HSO\(_4^-\) > ClO\(_4^-\) > Cl\(^-\).\(^{29}\) The ion with smaller hydration radius can access those sites, which are inaccessible to ions with larger hydration radius, and would yield a higher value of the maximum charge storage capacity.

Charge storage characteristics of the leucoemeraldine band.—Oxidation of the film can only begin when the film is sufficiently polarized. The critical amount of charge which must be accumulated at the point of transition from leucoemeraldine to polaron band can be obtained by the construction shown in Figure 7. Here we have extended the best fit straight lines representing the polaron band backward, and found out the charge at which the coulograms deviate from these straight lines. Thus we have located the points at which the leucoemeraldine band transits into the polaron band. The horizontal dotted line connects all these points. This shows that there is a fixed charge density which must be reached before faradaic charging of the film begins. We call this the ‘faradaic threshold’. It appears to be independent of the concentration of the acid.

We also find that the electrode potentials at the faradaic threshold are different for different concentration of acids. For 5 mM acid, the potential is highest. This is understandable since the capacitance of the leucoemeraldine band for this concentration is lowest. However, what is surprising is that the threshold potential is the least in 95 mM acid. A possible explanation for this behavior is that as the film is polarized, it swells and its capacitance increases. This explains the marked curvature of the coulogram in the later part of the leucoemeraldine band. The threshold potential is determined by the composite effect of the capacitance of the film and osmotic driving force. The former...
increases, but the latter decreases with increase in concentration of the acid. In 95 mM acid both factors are favorable and hence it shows the lowest threshold potential.

Comparison with linear sweep voltammetry.— Cyclic voltammetry experiments were performed at different sweep rates. For a given sweep rate, a sequence of experiments was conducted in which, the base potential was held at −0.2 V and the end potential was increased in steps of 12 to 13 mV. Multiple cycles were performed in each CV experiment until the cyclical steady state was achieved and only the last cycle was used for the analysis. The charge stored in the film was obtained by dividing the area under current-potential plot by the sweep rate. The stray charge was eliminated by taking the arithmetic mean of the absolute charge stored during the forward and the reverse sweeps, based on the reasoning that the stray current does not change sign during the forward and reverse sweep, but the charging current does change sign.

Figure 8 shows sweep coulograms (plots of the specific charge density stored in the film, \( q_f \), versus the end potential) at different sweep rates. All experiments were conducted in 95.2 mM sulfuric acid, on films with \( ip = 35.2 \text{ A.m}^{-2} \). The step coulogram under identical conditions is also presented in Figure 8a (shown by the black squares).

The sweep coulogram, obtained at low sweep rate (e.g. \( v = 50 \text{ mV s}^{-1} \)) is shown in Figure 8b. It reveals five bands. However, from Figure 8a, we see that the number of bands reduces with increase in the sweep rate, that is, we see 3-bands at \( v = 1 \text{ V s}^{-1} \) and 2-bands at \( v = 2 \text{ V s}^{-1} \).

We also observe that at a fixed potential, the stored charge decreases with increase in the sweep rate. This is expected since several dynamic steps involved in the sweep voltammetry slow down the charging process. We expect the sweep coulogram to asymptotically approach the step (equilibrium) coulogram as the sweep rate tends to zero. Since polaron band persists for all sweep rates, we study dependence of the capacitance of polaron band, \( c_{fp} \), on the sweep rate. We find from Figure 9 that \( c_{fp} \) varies as \( \sqrt{v} \). The points corresponding to the step coulograms, \( (C_{fp})_{step} \), are shown at \( v = 0 \). All plots pass through \( (C_{fp})_{step} \) at \( v = 0 \).

Figure 10 shows a part of the sweep coulograms spanning leucoemeraldine and polaron regions. A construction similar to that in Figure 7 has been carried out in Figure 10 and the faradaic threshold is determined. We see from this figure that the faradaic threshold is identical to that in Figure 7. This indicates that the faradaic threshold is independent of scan rate. Therefore it is an intrinsic property of the film.

The lowest threshold potential is exhibited by the step coulogram. The sweep coulograms exhibit higher threshold potentials, which incomparable, but the latter decreases with increase in concentration of the acid. In 95 mM acid both factors are favorable and hence it shows the lowest threshold potential.
crease with increase in the sweep rate. This is not surprising since at higher the sweep rate, shorter is the time needed to reach the given end potential and hence smaller is the quantity of the charge accumulated during sweep. Thus a greater value of the end potential is needed to charge the polymer to the same charge density at higher sweep rate.

Conclusions

We have developed a step voltammetry technique to estimate equilibrium charge storage characteristics of a polyaniline film. This technique is general and should be applicable to other conducting polymers. Using this technique we have detected the five energy bands of polyaniline film and determined differential capacitance and transition potentials of these bands. The film behaves as a linear capacitor in each energy band. We have also compared the equilibrium charge with that stored by the film during the linear sweep voltammetry. The latter decreases with increase in the sweep rate. The sweep coulogram shows five energy bands at low sweep rates. The number bands reduce as the sweep rate is increased. We find that the capacitance of the polaron band of the sweep coulogram varies with square root of sweep rate and attains the capacitance of the step coulogram at zero sweep rate. The faradaic threshold represents the points at which transition from leucoemeraldine band to polaron band occurs. The lowest threshold potential is exhibited by the step coulogram. The sweep coulograms exhibit higher threshold potentials, which increase with increase in the sweep rate. However the threshold charge is independent of both sweep rate and type of acid.

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