Electrochemical studies on doping of polyacetylene

C. K. Chiang*, E. A. Blubaugh† and W. T. Yap†
National Bureau of Standards, Washington, DC 20234, USA

(*Received 8 October 1983; revised 10 January 1984*)

The mechanism for electrochemical doping of polyacetylene was studied using cyclic voltammetry. The *I–V* curve of a thin $(CH)_x$ film (<1 μm) electrode exhibited a redox peak with a formal redox potential of $+0.65$ V vs. sodium calomel electrode. Approximately 30% of the total charge that oxidized $(CH)_x$ was not reversible when held at the open circuit voltage of the cell. A more negative potential was needed to recover the remaining charge. This large charge-trapping phenomenon was the consequence of the $(CH)_x$ film being doped. Using a thick film ($\gtrsim 50\,\mu m$) electrode or freestanding film (~ 0.1 mm) as an electrode, the *I–V* curve gave only a broad re-reduction peak at $+0.4$ V. The disappearance of the well-defined redox peak implies that the redox process revealed by the thin film data may not be the predominate mechanism for the doping process.

(Keywords: polyacetylene; electrochemistry; doping; cyclic voltammetry; conducting polymer; redox process)

INTRODUCTION

Recent investigations on conducting polymers have indicated that the conductivity of certain polymers can be enhanced many orders of magnitude by doping with a variety of chemical species[1-4].

The process of adding a small quantity of selected chemical species into a polymer to achieve the control of its electrical and electronic properties is 'doping'. The chemical species are dopants. The concept of doping is borrowed from the field of conventional semiconductors. It is used to describe the changes in electronic structure of the polymer due to a small amount of added chemical impurity[5]. The dopant concentration in the conducting polymers is several orders of magnitude higher than that found in conventional semiconductors. Although it is clear that the doping process is extended far outside its original definition, the physical properties of these conducting polymers are closely analogous to those found in conventional semiconductors. Polymers with properties of metals and semiconductors will certainly have important impact on future industries. The foundation of these properties lay on the doping process. Hence, the understanding of the doping phenomena is fundamental for the research of conducting polymers.

It also has been shown that the doping of a polymer could be accomplished by an electrochemical method[6-10]. This synthetic method was further investigated in an electrochemical study[11]. In the electrochemical synthesis of doped polyacetylene, a constant voltage (as large as 9 volts) or current was applied to an electrochemical cell. These experiments were designed to obtain high dopant concentration and high conductivity for polyacetylene. There was little electrochemical information associated with the doping process. On the other hand, the electrochemical studies show that pure polyacetylene has redox sites as indicated by presence of the electrochemical peaks in the cyclic voltammogram. The polymer did become more conductive after oxidation. These experiments suggest that the doping is an oxidation or reduction process. However, a redox process that can give such substantial alternation in the physical properties of polymer, should be a class in and of itself and requires special attention. A close analogue is the intercalation of graphite.

Here we present some well defined electrochemical data for undoped, partially doped and heavily doped polyacetylene. These data provide support for interpreting a doping process as a specific type of redox process. Polyacetylene is used here because it is a model conducting polymer with prototype behaviour of doping.

EXPERIMENTAL

Polyacetylene was synthesized using the polymerization technique as described in the literature[12,13]. The polyacetylene film electrodes were made in the same manner. The surface of platinum electrode which was first coated with catalyst solution. The polymerization of acetylene gas occurred on that surface. The entire procedure was carried out in vacuum. The thickness of the film was controlled by gas pressure and polymerization time. Typical thickness of the thin polyacetylene film electrodes and the thick polyacetylene film electrodes were $\sim 1\,\mu m$ and $>50\,\mu m$, respectively. A thin *trans* $(CH)_x$ film electrode showed a blue reflection from the platinum substrate. The thicker $(CH)_x$ film electrode appeared to be dark brown which is similar to the dull side of the (free standing) film. We also made some electrodes using (free standing) polyacetylene films of 0.1 mm in thickness. The electrical contacts to these (free standing) film electrodes

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* Polymer Division.
† Organic Analytical Chemical Division.

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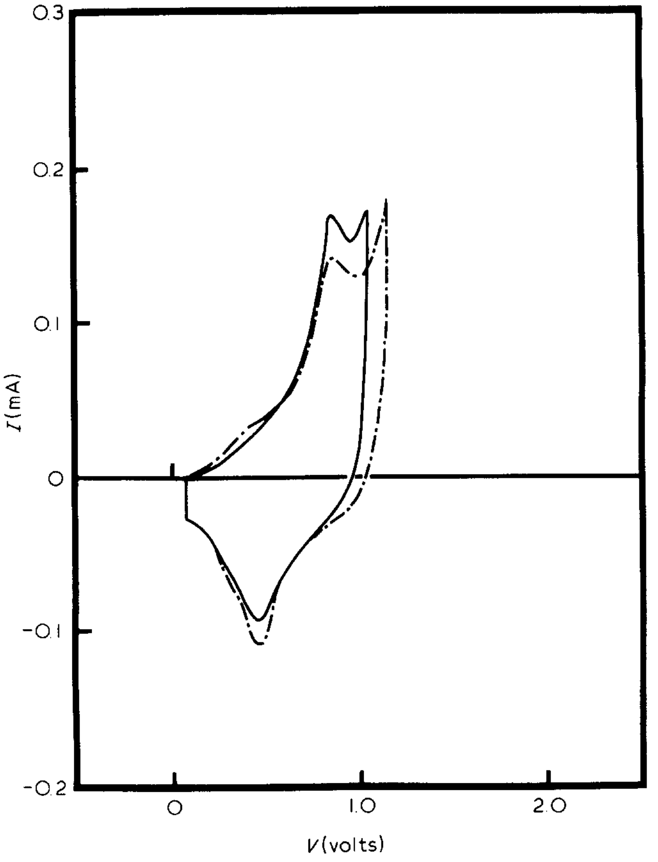

Figure 1 Cyclic voltammogram of a thin *trans* $(CH)_x$ film electrode: the solid line is the first scan, the broken line is the 3rd scan of the same electrode. (Scan rate 20 mV/s; Supporting electrolyte: 0.5 mol l^{-1} TEAP in propylene carbonate)

were made by pressure contacts of platinum sheets at one end of the film.

Only one surface (0.23 cm^2) of the electrode was covered with polymer. The other size of the electrode was insulated. Several supporting electrolytes were used: Tetraethylammonium perchlorate (TEAP), lithium hexafluoroarsenate ($LiAsF_6$) and lithium perchlorate ($LiClO_4$) in propylene carbonate or acetonitrile. The solutions were de-oxygenated in an argon atmosphere. The concentration of supporting electrolyte ranging from 0.1 to 0.5 mol l^{-1} were used. No noticeable change in electrochemical behaviour was found when using different supporting electrolytes or using different concentrations. Description of the electrochemical measurement system and air-tight nonaqueous cells used in this work has been published elsewhere[14]. The potentials were measured against a saturated sodium calomel reference electrode (SSCE). No IR-drop compensation was made for these measurements. The IR-drop compensation was not used since the conductivity of the polymer would be changing during the voltage application.

These $(CH)_x$ films were characterized using infrared spectrum and electrical conductivity. Since our primary interest is in the mechanism of doping, extremely high purity films are not required. In fact, the doping can occur in $(CH)_x$ film in a wide quality range. Only when one likes to obtain very high conductivity or some well defined low doping state, the quality of the film becomes important. However, we have made all possible precautions for preserving the $(CH)_x$ film in the electrochemical cell.

RESULTS

The cyclic voltammogram for a thin *trans* polyacetylene film electrode in 0.5 mol l^{-1} $LiClO_4$ propylene carbonate solution is shown in *Figure 1*. The oxidation of $(CH)_x$ is well defined with a peak potential $E_{pa} = +0.85$ volts. A shoulder is observed at +0.45 volts. The reduction of the oxidized sites is seen in the reverse scan, which gives a well defined peak potential at $E_{pc} = +0.45$ volts. Also, a shoulder is found at +0.30 volts. A rather large background current is seen. The first scan of the cell is always different from those of subsequent scans. The E_{pa} of the first scan is at slightly higher potential and shows greater current than later scans. After the first scan the shape of I–V curves change slowly with each re-cycle. The redox couple peaks shown in *Figure 1* have a rather large potential difference, $\Delta E_p = E_{pa} - E_{pc} = 400$ mV. A freshly prepared undoped film electrode had an open circuit voltage $V_{oc} = +20$ to $+60$ mV. The V_{oc} jumped to +350 mV after the first scan. The maximum open circuit voltage we have seen was in the range +600 mV to +800 mV.

To simulate the doping process, the following experiment was performed. A fixed potential (1 volt) was maintained on the cell for a fixed amount of time and the total charge transferred was measured. The cell potential was then reset to its original open circuit voltage, and total discharged charge was measured again. The reversibility of the cell was defined as the ratio of the charges involved during charging and discharging. For the electrode from which the voltammogram of *Figure 1* was obtained, the reversibility was 72%. To recover 100% of the charge, a more negative potential is required. Thus we believe that the reversibility of the redox process in undoped $(CH)_x$ is at 60–75%.

Figure 2 shows the cyclic voltammogram of a thick $(CH)_x$ film electrode in 0.25 mol l^{-1} TEAP propylene carbonate solution. Over the same potential range as before we did not find a well defined oxidation peak. The background current has substantially increased. If one examines the I–V curve closely, there is a slope change beginning at the potential $E+0.4$ volts. When the scan reversed we observe a broad reduction process peaked at $E_{pc} = +0.4$ volts. Measurement of the reduction peak size (the peak size refers to the height of peak with background subtracted) as function of scan reveals that the peak size increases as the square root of scan rate as shown in *Figure 3*. This suggests the reduction process is diffusion controlled.

Continued cycling of the thin $(CH)_x$ film electrode between fixed potentials shows the peaks E_{pa} and E_{pc} are reduced in size. This effect is illustrated in *Figure 4*. The I–V curve gradually lost its characteristic peaks over a period of 8–20 h. The width of splitting between the positive and negative scans became narrow and disappeared eventually. For thick $(CH)_x$ film electrode, on repeated scanning the E_{pc} first shifts to less positive potential and then back to the same potential. The peak height was increased when the E_{pc} decreased and the peak size decreased with the E_{pc} increases. Continued cycling between two fixed positive potentials, we found the same response as described for the thin film case. The electrochemical behaviour of a free standing film electrode show identical characteristics as those described for the thick $(CH)_x$ film electrode.

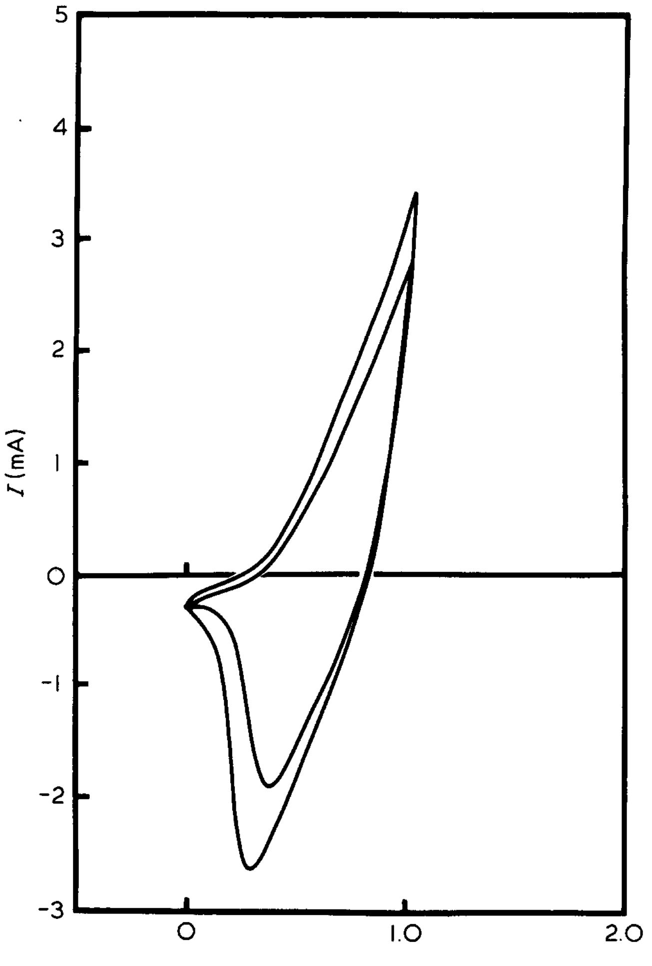

Figure 2 Cyclic voltammogram of a thick *cis* $(CH)_x$ film electrode. The larger peak is the first cycle. The smaller peak is the 4th cycle. (Scan rate 20 mV/s; supporting electrolyte: 0.25 mol l^{-1} TEAP in propylene carbonate)

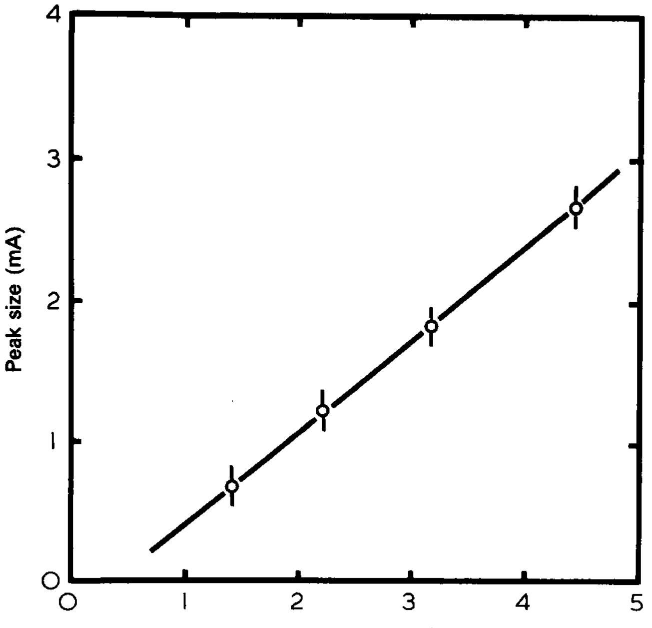

Figure 3 Height of the reduction peak of a thick *cis* $(CH)_x$ film electrode as function of scan rate

A heavily droped $(CH)_x$ film electrode was made *in situ* in the electrochemical cell using AsF_5 gas as dopant. The cyclic voltammogram of the AsF_5 doped $(CH)_x$ film electrode is shown in *Figure 5*. This I–V curve has no characteristic peaks, but a 'football' shape. The 'football' shape I–V curve was thinner after 14 h of repeat cycling.

DISCUSSION

To obtain useful information from a polymer electrode one normally needs very thin polymer coating. This is because the conductivity of a typical polymer is on the order of 1×10^{-16} ohm^{-1} cm^{-1}. However, polyacetylene is a semiconducting polymer: The conductivity of pristine *cis* $(CH)_x$ and *trans* $(CH)_x$ are 1×10^{-9} ohm^{-1} cm^{-1} and 1×10^{-5} ohm^{-1} cm^{-1}, respectively. Given a fixed electrical resistance the $(CH)_x$ polymer electrode can be much

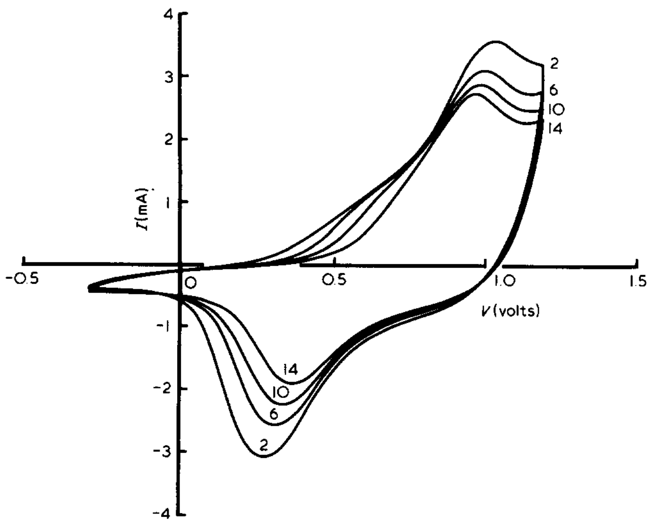

Figure 4 Variation of peaks of a $(CH)_x$ film electrode under continuous cycling between two fixed voltages. The numbers near the curve are the counter of the cycles. (Scan rate: 100 mV/s; supporting electrolyte; 0.1 mol l^{-1} TEAP in CH_3CN)

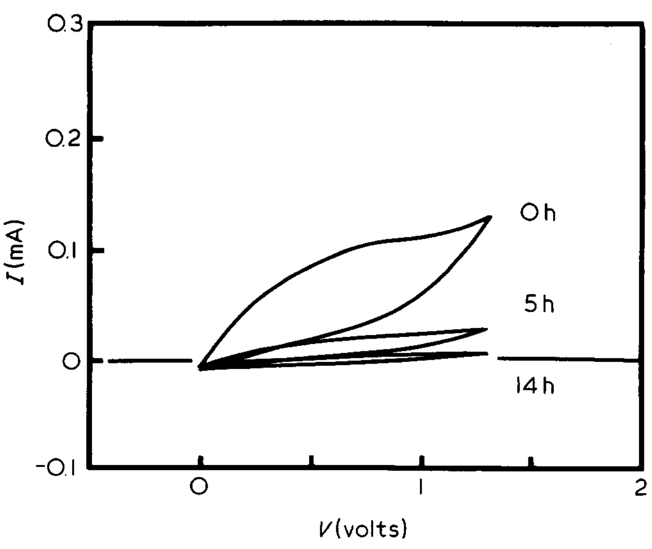

Figure 5 Cyclic voltammogram of a AsF_6 doped $(CH)_x$ electrode. The time indicated is the time that the I–V curve was traced. The electrode voltage was cycling between 0 and 1 volt throughout the experimental period. (Scan rate: 20 mV/s; supporting electrolyte: 0.5 mol l^{-1} $LiAsF_6$ in propylene carbonate)

thicker than that of a typical insulating polymer. The cyclic voltammograms of $(CH)_x$ obtained using film of 100 μm in thickness are still valid, and do not have large distortion due to high resistance. Experimentally, by comparing *Figures 1* and *2*, we observed a small shift of 0.05 volts for the re-reduction peaks, while the resistance of these two $(CH)_x$ films differ by at least 1000 times. These results are not only consistent with the high conductivity nature of $(CH)_x$, but also rule out the possibility of an *IR*-drop as the major contribution to the observed data.

For thin $(CH)_x$ electrodes our data are in good agreement with the earlier report[11]. The main features are: (1) non-symmetric redox peaks, (2) large reduction peak, (3) high slope in oxidation current even at potential higher than oxidation peak. The open circuit potentials extracted from these experiments are consistent with the results of battery experiments[6–9]. Using a free standing $(CH)_x$ film evaporated with 500 Å gold metal Nigrey *et al.*[10] obtained a cyclic voltammogram which resembles *Figure 1*. In fact, we judge that the data is a typical thick $(CH)_x$ electrode behaviour. We argue that they observed a peak difference $\Delta E_p \sim 1.0$ volts, which is much larger than that observed in a thin film electrode, $\Delta E_p \sim 0.3$ volts. If we line-up the re-reduction peak at +0.4 volts as we found in *Figure 2*, their oxidation peak is at +1.4 volts. The continuing oxidation beyond +1.0 volts has been noticed by Diaz and Clarke[11]. Our experience indicated that the peaking of oxidation current beyond 1.0 volts appears to be caused by extrinsic factors. The intrinsic behaviour of thick $(CH)_x$ electrode is well defined below 1.0 volts. Hence, we conclude that the cyclic voltammograms of the thick film and standing film $(CH)_x$ resemble that of the thin film except the oxidation peak $E_{pa} \sim 0.85$ volts is absent in the same potential range.

Continuously cycling the electrode potential between 0 and 1.0 volts is effectively equal to the interrupted doping using gaseous dopant. A pulse potential should be better for producing a well defined oxidation leve. Since there are 30% ions (i.e. charges) remaining in $(CH)_x$ film after each cycle, the film is considered slowly doped. The variation of oxidation peak reflects the change of conductivity and structure. The decrease of the peak size suggests that the number of available oxidation sites is reduced. When the $(CH)_x$ film was heavily doped, we observed no peaks as shown in *Figure 5*. But the shape change of *I–V* curve suggests the doping still occurring. Thus, we propose that the observed $E_p \sim 0.85$ volts may no directly represent the doping phenomena.

Let us return to the characteristics of the behaviour of a thin $(CH)_x$ electrode. The fact that both large current and high slope appear at the same time in the $(CH)_x$ electrode suggests this is not a typical electrochemical response[15,16]. If the background current was due to the effect of *IR*-drop, one would expect an increase in the slope and a decrease in current when the film thickness is increased. The shape of the *I–V* curve should vary correspondingly. Experimental results shown in *Figure 2* indicate that the general shape of the cyclic voltammogram of thick $(CH)_x$ film remains unchanged while the electrical current was increased by about 20–30 times. The magnitude of the current is approximately scaled to the thickness of the $(CH)_x$ film. It suggests that the electrochemical processes occurred throughout the volume of the film, not just on the surface of the electrode. This phenomena is consistent with the fact that the $(CH)_x$ film has only 1/3 of its theoretical density[12,13]. The two thirds of empty volume allows the supporting electrolyte to reach the surface of all the fibres of the film. Hence, we would have much more active area than that defined by the flat platinum surface. The large area gives larger electrode capacitance, and in turn produces a high slope in the *I–V* curve. More area allows more electrochemical reaction and results in a huge current.

The electrochemical reaction occurs over the surface of all fibres then the reaction should be controlled by diffusion through empty space of the film. This explains the results shown in *Figure 3*. Also, the oxidation peak E_{pa} observed in the thin $(CH)_x$ electrode should increase its magnitude at the vicinity of 0.85 volts when the thickness of the film increases. However, *Figure 2* does not show a large oxidation peak at that potential. The absence of a large peak at 0.85 volts again suggests the peak is not directly related to the current we discussed earlier. In other words, it may be a separate electrochemical process. And this process should be a process which will not increase with the volume of the $(CH)_x$ film.

The above experimental results may be consistent with that of the electrochemical behaviour of $(CH)_x$ film electrode composed of two processes. One process which dominates in thin film electrodes is a simple electrochemical redox response. The other process which dominates in thick film electrodes is a doping process. The simple redox process occurring on the very surface of platinum substrate, has an asymmetric *I–V* shape as shown in *Figure 1*. While the source of this redox is not well identified, we may assume it is the oxidation of the double bonds, C=C, in the $(CH)_x$ when it is located immediately to the platinium. The doping process which can occur over whole $(CH)_x$ sample, is represented as *Figure 2*. The shape of the curves closely resemble that found in intercalation of graphite[17]. The close correspondence between the $(CH)_x$ polymer and graphite has been seen in many properties[4,18]. Here we could interpret the large current observed to be the result of a reaction similar to the interclation of graphite. This implies that the ions or dopants indeed migrate into the interior of $(CH)_x$ fibres.

Now we attempt to describe the electrochemical reactions which can lead to these observed *I–V* results. A simple redox reaction in the $(CH)_x$ electrode can be written as

$$(CH{=}CH) \leftrightarrows (CH{=}CH)^{\dot{+}} + e^- \qquad (1)$$

where (CH=CH) is a monomer of $(CH)_x$. The redox process of the carbon–carbon double bonds is well known[15]. This redox reaction occurs only very close to the metal interface of the electrode, so that the electrons can be removed quickly. The ionization potential for equation (1) is approximately +0.65 V with respect to a sodium calomel electrode, or +0.89 V with respect to a hydrogen electrode.

Since the electrons in $(CH)_x$ chain can be easily delocalized, equation (1) is modified as follows.

$$(CH{=}CH)_n \rightleftharpoons (CH{=}CH)_n^{\dot{+}} + e^- \qquad (2)$$

The term $(CH{=}CH)_n^{\dot{+}}$ represents that the one charge for the electrochemical reaction does not come from any particular localized carbon–carbon double bond, but from the set of *n* adjacent conjugated bonds. Here *n* is an integer larger than one and smaller than the number of (CH=CH) units in the chain. The dispersion of charge through *n* units of monomer is consistent with the concept of doping and also the electrochemical reaction. Since *n* is a variable, one would not expect to have a fixed ionization potential. Following the ionization to $(CH{=}CH)_n^{+}$ the polymer can be doped with charged dopant ions, ClO_4^-, for example

$$(CH{=}CH)_n^{\dot{+}} + (ClO_4)^- \rightleftharpoons [(CH{=}CH)_n{}^+(ClO_4)^-] \quad (3)$$

The term $[(CH{=}CH)_n{}^+ClO_n{}^-]$ describes a single dopant ion associating with the $(CH)_x$ polymer segment. Using conventional notation $[(CH)(ClO_4)_y^-]_x$ for doped $(CH)_x$, we have $y = 1/n$. Since equation (3) follows immediately after equation (2), the reaction will continue with no peaking unless limited by extrinsic conditions. Under suitable conditions, the doped polymer can be reversed.

$$[CH{=}CH)_n{}^+(ClO_4)^-] + e^- \rightleftharpoons (CH{=}CH)_n + (ClO_4)^- \quad (4)$$

Equation (4) is the response to the large re-reduction peak shown in *Figure 2*. Equations (2) to (4) describing the electrochemical response of the $(CH)_x$ film is similar to the classical case of silver electrode reaction in the presence of Cl^- ions. Further implication of these relations are currently under evaluation.

CONCLUSION

We have examined the electrochemical behaviour of polyacetylene film using cyclic voltammetry. The *I–V* curve of a $(CH)_x$ electrode with a film thickness less than 1 μm exhibits an oxidation peak at +0.85 volts and a reduction peak at +0.45 volts, both potentials are measured against sodium calomel standard electrode. In an experiment that simulates doping of $(CH)_x$ we found approximately 30% of the total charge that oxidized $(CH)_x$ was not reversible when the cell was held at the open circuit potential. A more negative potential is required to recover the remaining charge. This large charge-trapping phenomena is the consequence of $(CH)_x$ film being doped. Using a $(CH)_x$ electrode with the film thickness $\gtrsim 50$ μm we observed a broad reduction peak at +0.40 volts with over all current scaled up about 30 times. The oxidation peak at +0.85 volts was absent. The disappearance of the well-defined redox peak implies that the redox process revealed by the thin film data may not be primary mechanism for doping of $(CH)_x$. Taking into account of the electron delocalization in $(CH)_x$ chain and the concept of doping, we proposed a mechanism which contains two processes. One of them is considered as doping with characteristic behaviour like silver in the presence of Cl^- ions.

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