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Polyaniline films electro-deposited from acidified non-aqueous media were investigated for their electropolymerization behavior and charge-discharge characteristics. The solution system used for the electropolymerization of polyaniline films was CF_3COOH acidified propylene carbonate, which was previously found to be the best system for the preparation of highly electroactive conducting polymer film. Electroactive polyaniline films only form in solutions wherein the mole ratio of acid (CF_3COOH) to aniline monomer is greater than one. As the acidity is increased, the resultant polyaniline film exhibits greater electroactivity and better charge-discharge performance. This affect may be ascribed to the higher porosity and, therefore, larger surface area that forms at the higher rates of polymerization in the high acid content solutions.

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Electroactive Polyaniline Film deposited from Non-Aqueous Media
2: Effect of Acid Concentration in Solutions

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Abstract

Polyaniline films electro-deposited from acidified non-aqueous media were
investigated for their electropolymerization behavior and charge-discharge characteristics.
The solution system used for the electropolymerization of polyaniline films was CF_3COOH
acidified propylene carbonate, which was previously found to be the best system for the
preparation of a highly electroactive conducting polymer film. Electroactive polyaniline
films only form in solutions wherein the mole ratio of acid(CF_3COOH) to aniline
monomer is greater than one. As the acidity is increased, the resultant polyaniline film
exhibits greater electroactivity and better charge-discharge performance. This affect may
be ascribed to the higher porosity and, therefore, larger surface area that forms at the higher
rates of polymerization in the high acid content solutions.

Electrodes modified by electro-deposited polyaniline(PAn) films have been investigated extensively in recent years(1-11). Such polymer-coated electrodes may be applicable to a wide range of practical devices such as capacitors, polymer batteries, ion switching devices and electrochromic devices. Polyaniline is one of the most promising materials because of its high doping level(> 50-80%) and fast switching rate. Many investigation of the electropolymerization of aniline in aqueous solutions using several different strong acids, including H_2SO_4, HNO_3, HCl, HBF_4, $HClO_4$, and CF_3COOH, have been attempted(6-9). However, the electrodeposition of polyaniline out of non-aqueous media has only been reported by the present authors(1,2).

In previous investigations, the polyaniline films deposited from non-aqueous solutions with an organic acid(CF_3COOH) of appropriate electrolyte content were highly electroactive and porous, with larger charge capacity and higher rate capability than those deposited from acidic aqueous solutions(1(a)). In non-aqueous solutions, it is possible to avoid the nucleophilic attack of OH⁻ on the radical cation initiators and thus produce polymer films more efficiently. To acidify a PC (propylene carbonate) solution without decomposing it at the same time, we tried the following five acids whose pKa values varied stepwise(1(b));.three inorganic acids: perchloric acid($HClO_4$), sulfuric acid(H_2SO_4), hydrochloric acid(HCl) and two organic acids: trifluoro acetic acid(CF_3COOH) and , acetic acid(CH_3COOH). In the presence of : HCl or $HClO_4$, hydrogen gas was evolved due to hydrolysis of the PC and a cathodization in the presence of the 30-40% of water which inevitably exists in these acids. In the case of the H_2SO_4/PC solution, anilinium salts(($Ph-NH_3$)$_2SO_4$) were readily precipitated. By using acetic acid or trifluoroacetic acid, the PC solvent could be acidified without any hydrogen evolution and an electroactive PAn was successfully deposited.

The present paper reports the effect of the relative concentrations of acids and aniline monomers on the enhancement of the charge-discharge characteristics at the polyaniline cathode in a lithium cell.

Experimental

Solutions and Film Preparation

Polyaniline films were deposited on a platinum substrate by the electro-oxidative polymerization method, with either a controlled-current or a scanned potential between -0.7 and 0.4 V *vs.* a silver/silver ion(0.01 mol dm^{-3} AgNO$_3$) reference electrode in the same solution. The scan rate was 10 mV s^{-1}. The solutions contained 0.5 mol dm^{-3} aniline monomer, 0.5 mol dm^{-3} LiClO$_4$ and various kinds of acids. The PC solvent and the salt were purified using standard methods described elsewhere(1).

Electrochemical Measurements

The polymerization behavior was analyzed by both consecutive cyclic voltammetry and a controlled current electropolymerization measurements on a Pt substrate. Charge-discharge tests were carried out on a Li/1.0 mol dm^{-3} LiClO$_4$(PC)/PAn cell where the polyaniline was prepared with a loading of up to 20 C cm^{-2}. The morphology of the polyaniline films formed with 5 C cm^{-2} was inspected by scanning electron microscopy.

Results and Discussion

Electrochemical Polymerization Behavior

By using trifluoroacetic acid, the acid content was varied while maintaining the aniline monomer concentration at 0.5 mol dm^{-3}, and the subsequent polymerization was observed over the voltage range from 0.2 to 0.4 V. As shown in Fig.1a), when the acid content also was 0.5 mol dm^{-3},i.e., the monomer/acid ratio=1, electroactive polyaniline was not formed. As long as the ratio of aniline monomer to acid was greater than 1:2(see Figs. 1a) and 1b)), currents due to the oxidative-polymerization of aniline became lower

with increasing cycle number. This suggests the film was not very conductive.

However, when the ratio was less than or equal to 1:2(see Figs.1c) and 1d)), an electrically conducting and electrochemically active polyaniline film was continuously formed. Furthermore, when the ratio was 1:4 the resulting film exhibited a very high electroactivity. The peak currents in the 1:4 ratio solution were twice those in the 1:2 ratio solutions and more than five times greater than those in the less acidic solutions.

In the same solutions, we performed constant-current electropolymerization, and the electrode potential was observed against the lapsed time as shown in Fig.2. When the ratio was 1:1, the electrode polarized to a very high potential, and there were no electroactive polyaniline deposits on the substrate but just polyaniline oligomers dissolved into the solution. When the ratio was changed to 1:1.2, there was still a large amount of oligomer flow, but some polyaniline deposit was also observed on the substrate. In contrast, in the solution whose ratio was 1:1.6, there appeared two regions of current vs. time behavior, namely, polyaniline deposition on bare Pt, i.e., the initial monolayer formation, and the subsequent polyaniline growth. In terms of the charge under the first peak, it decreases with an increase in acid content, indicating that the polymerization reaction occurs smoothly in the more acidic solutions. Further, the polymerization potential becomes smaller when the monomer/acid ratio is decreased from 1:1.6 to 1:4. This means that the anilinium content becomes larger than the aniline monomer content in the solution.

One possible explanation is that the polymerization is initiated by the protonation of aniline to form an acid-base equilibrium between the nitrogen of the aniline and the proton. With an increase in acid content in the solution, the aniline monomer is more easily protonated and therefore, the polymerization reaction proceeds rapidly. Also, the equilibrium will shift towards the protonation of nitrogen in the polyaniline film, which makes the film more conductive.

The polymer yield(w/Q_f), or, polymerization efficiency was estimated by dividing the weight of deposited polymer by the charge passed during electro-polymerization. With

an increase in the acid content, the efficiency becomes higher and shows saturation in a solution containing more acid than 1:1.5(see Fig 3). In a solution whose monomer/acid ratio is less than 1:1.5, polyaniline did not remain on the substrate but would flow out into the solution. The discharge capacity of film per unit weight of formation charge(Q_d/Q_f) was also estimated. The Q_d/Q_f behavior shows similar change as that of w/Q_f. This suggests the number of reaction sites is proportional to the yield of polymer, and the number becomes larger for the film prepared in higher acidic solution.

Electrochemical Doping-Undoping Processes

Figure 4 shows a comparison of cyclic voltammograms(CV) for various PAn films of $1C\ cm^{-2}$ equiv. amount formed in various acidified PC solutions. The scan rate for these CVs were 50 mV/s. There is an enhancement of the reversibility of the electrode process with a fast anion motion within the PAn film upon increasing the acid content. From the scan-rate dependence of the CVs, the change of the rate-determining step of the PAn electrode was surveyed. We used the simple approximation that i_{pa} was proportional to some power X of scan rate(v), $i_{pa} \propto v^x$, this value was plotted against the acid content in solution, as shown in Fig.5. The electrode process seems to change from a diffusion-controlled region to a reaction-controlled region, indicating that the anion diffusion rate within these films becomes faster when the film is formed in a more acidified solution.

SEM Micrographs

Figure 6 shows SEM micrographs for aqueous and non-aqueous polyaniline films. Some differences in the morphologies of the two films are observed. The PAn film prepared in the aqueous $HClO_4$ solution has a fibrous structure. On the other hand, the film prepared in the acidified PC solution has a grainy structure, somewhat like that of polypyrrole films, as previously reported(12). This difference in the film structure may be due to the difference of the film growth rate and the polarity of the solvent. Such

enhancement in electrode kinetics can be ascribed to a rougher morphology of PAn film that results from the higher rate of formation in more acidic solutions. As shown by the top view of the SEM micrographs, the surface becomes rougher for the film formed in the more acidified solution.

Finally, we assembled cells with various types of PAn films and lithium electrodes, and charge-discharge tests were performed. As Fig.7 shows, a remarkable enhancement of the charge capacity of batteries was observed for PAn cathodes prepared in the more acidic solution. The behavior corresponds very well with to the cyclic voltammteric results.

Conclusions

Two main factors are considered to be necessary for obtaining electroactive PAn from PC or other non-aqueous solutions. One is the existence of protons from an organic acid whose acidity is as high as that of CF_3COOH. The other factor is the existence of sufficient concentration of electrolyte to enhance the ionic conductivity of the non-aqueous solution. With an increase in the acid content in solution, the polymerization efficiency as well as the electroactivity of PAn films show striking enhancement. Charge-discharge performance enhancement is expected for such PAn films deposited from non-aqueous solutions.
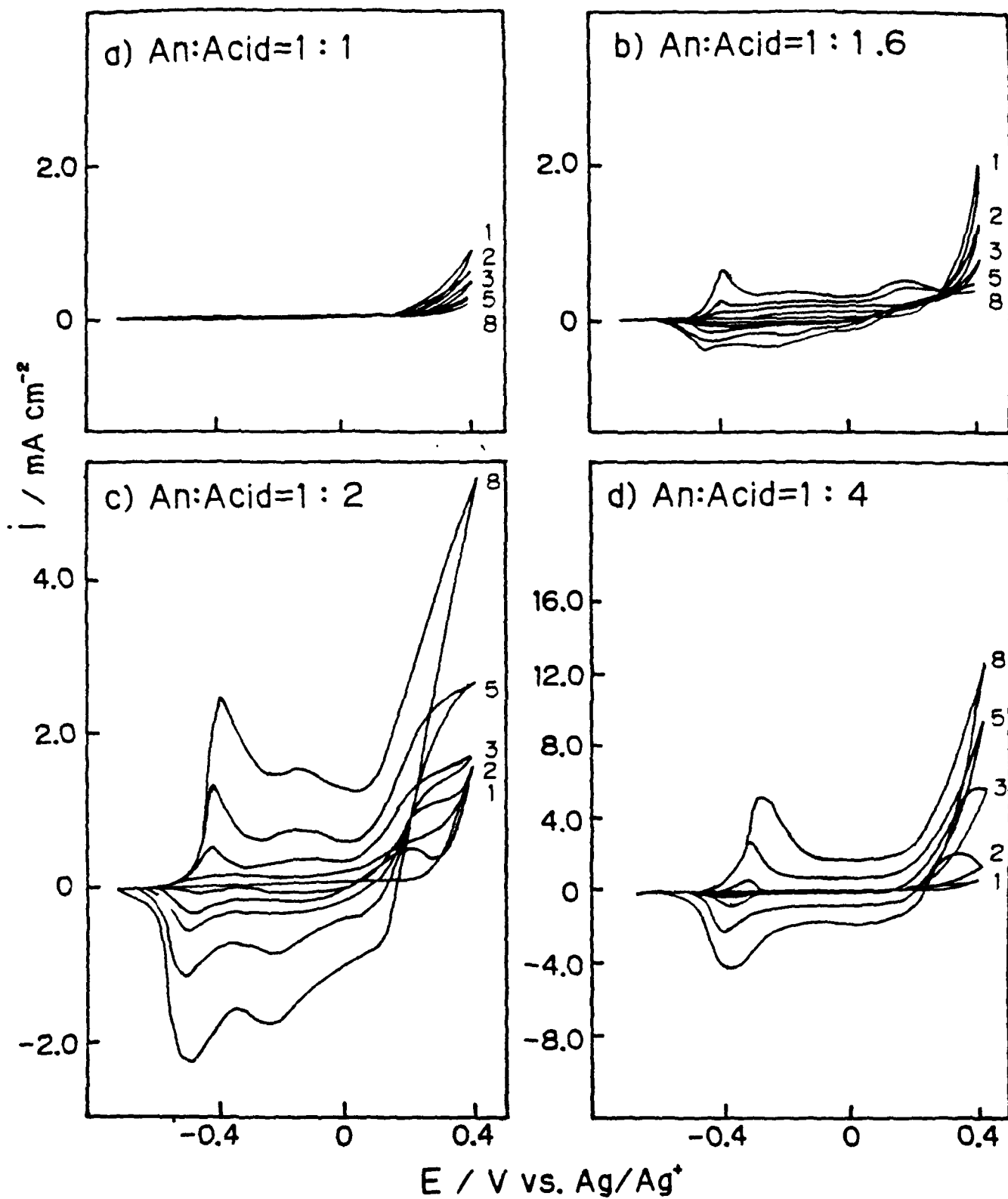
Acknowledgment

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Figure captions

Fig.1 Cyclic voltammograms for electropolymerization of aniline in PC solutions containing 0.5 mol dm^{-3} aniline monomer, 0.5 mol dm^{-3} $LiClO_4$ and various molarity(0.5 to 2.0 mol dm^{-3}) of CF_3COOH. Molar ratio of aniline monomer to acid are a) 1 : 1, b) 1 : 1.6, c) 1 : 2, and d) 1 : 4, respectively. (Cycle numbers are given in figures).

Fig.2 a) Potential vs. time curves during electropolymerization of polyaniline in (0.5 mol dm^{-3} aniline monomer + 0.5 mol dm^{-3} $LiClO_4$ + (0.5 to 2.0 mol dm^{-3}) CF_3COOH)/PC solutions under galvanostatic condition. b) Charge under the first nucleation peaks in a).

Fig.3 Correlation of w(weight of as-deposited 1 C cm^{-2} passed polyaniline film) and Qd for the same films against the ratio of aniline to acid in polymerization solutions.

Fig.4 Cyclic voltammograms for polyaniline films(1 C cm^{-2}) in 1.0 mol dm^{-3} $LiClO_4$/PC solutions at a scan rate of 5 mV s^{-1}.

Fig.5 Changes in the rate-determining stage for polyaniline films(1 C cm^{-2}) prepared in various solutions of various accidities.

Fig.6 SEM micrographs(top view) of polyaniline films(5 C cm^{-2}).

Fig.7 Effect of charge depth on the coulombic efficiency of charge-discharge curves for Li/$LiClO_4$(PC)/Polyaniline(20 C cm^{-2}) cells. The current density at charge-discharge test was 8 mA cm^{-2}.

a) An:Acid=1:1

b) An:Acid=1:1.6

c) An:Acid=1:2

d) An:Acid=1:4

i / mA cm^{-2}

E / V vs. Ag/Ag$^+$

Fig. 1

a) Legend:
- An:Acid = 1 : 1
- An:Acid = 1 : 1.2
- An:Acid = 1 : 1.6
- An:Acid = 1 : 2
- An:Acid = 1 : 3
- An:Acid = 1 : 4

Fig. 2

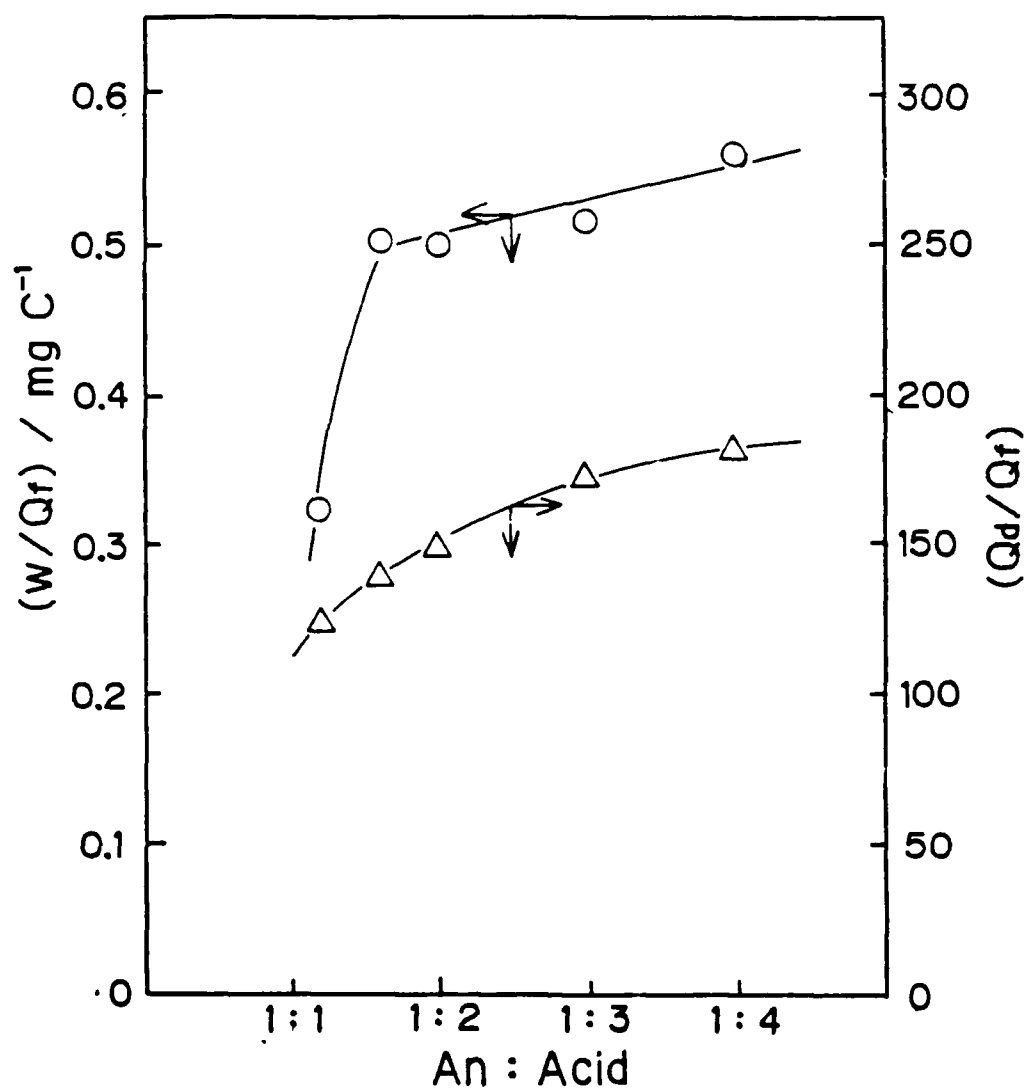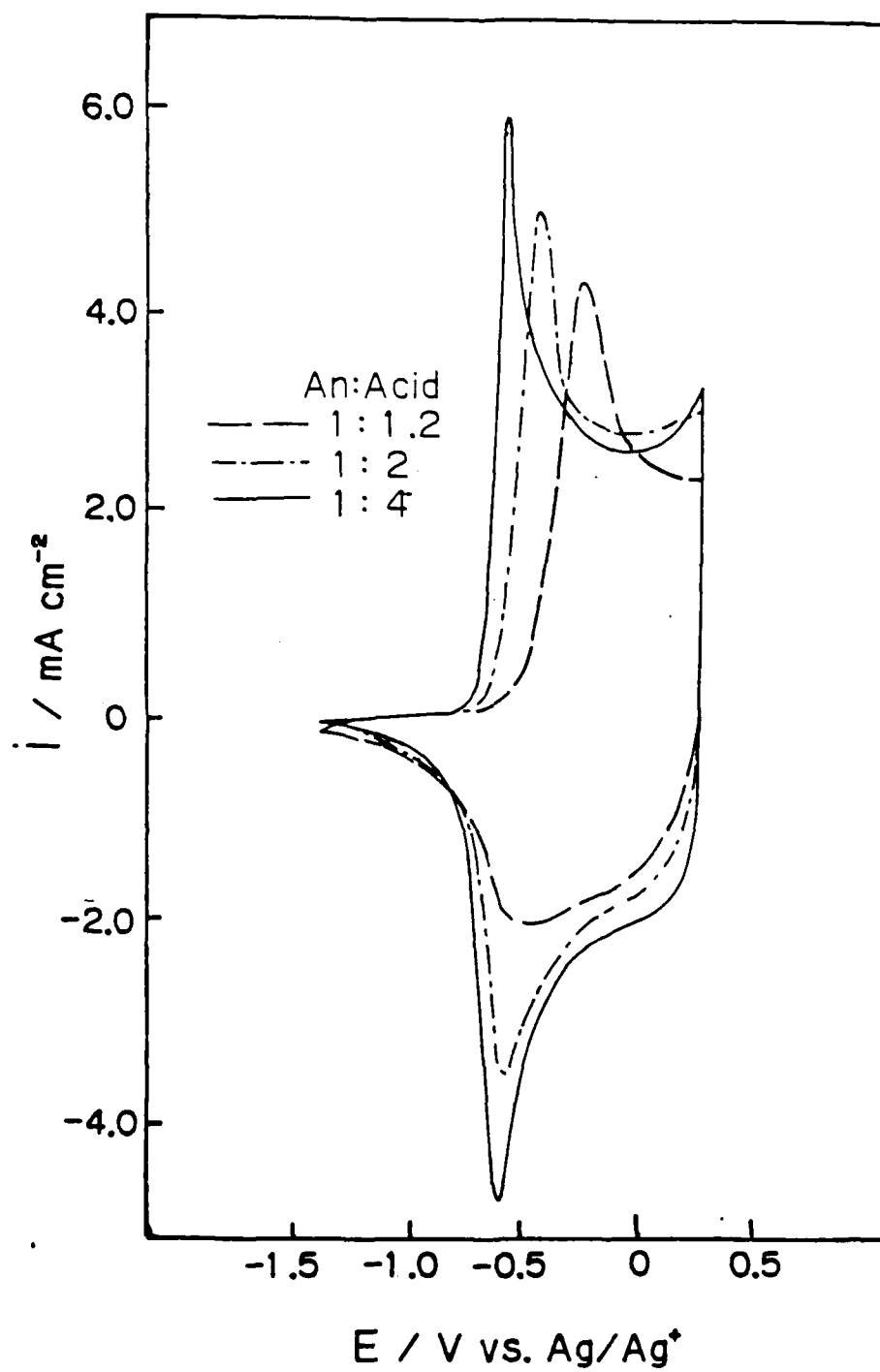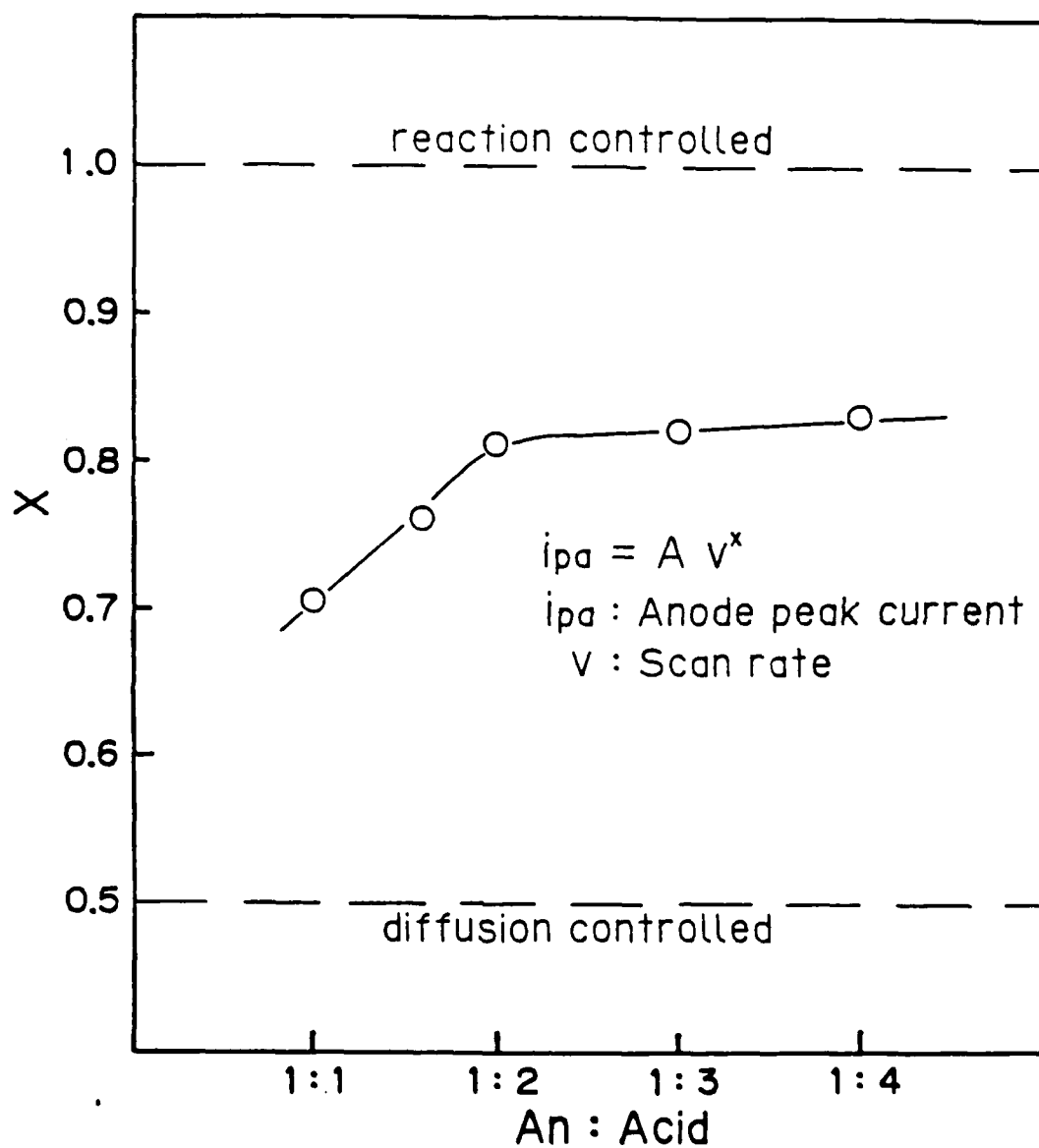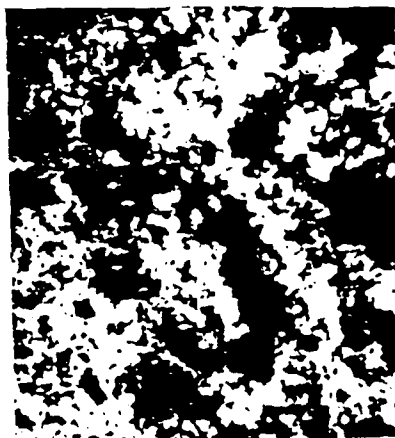Fig. 3

Fig. 4

Fig. 5

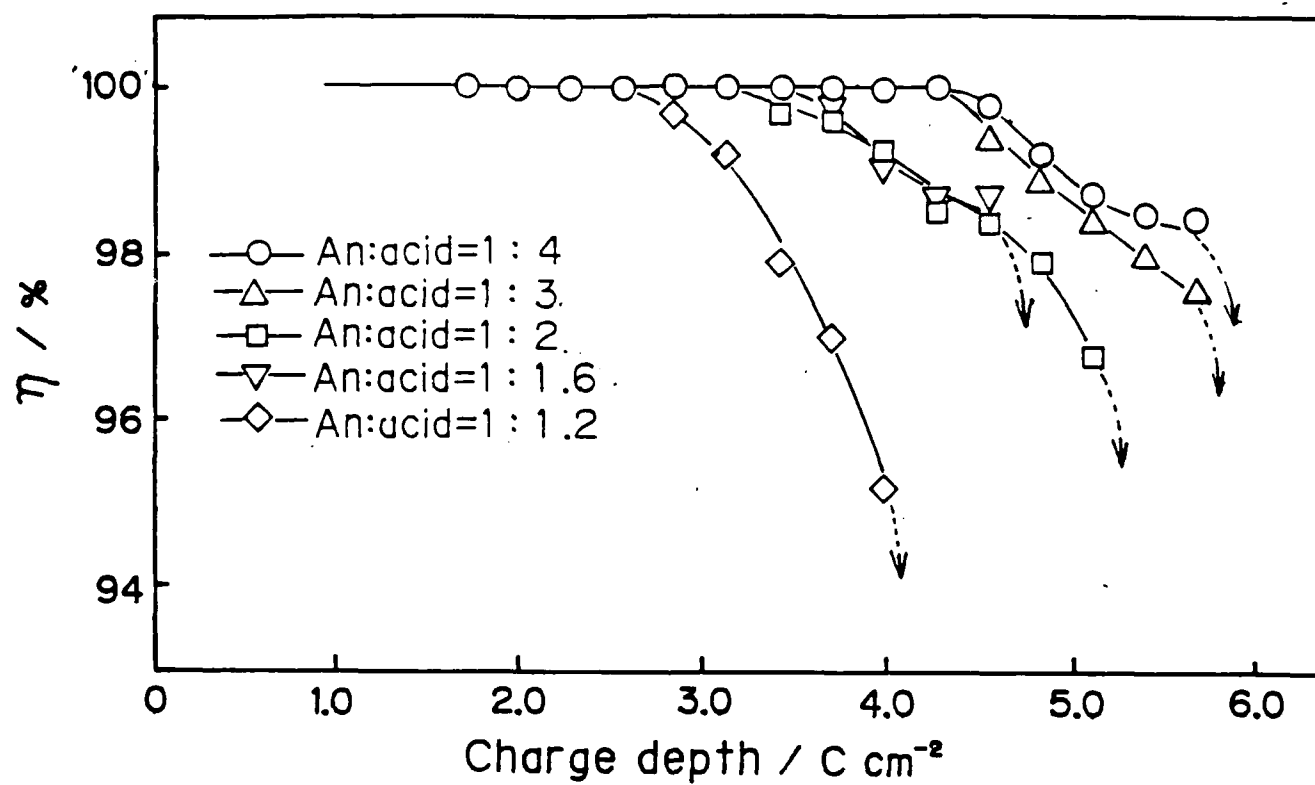a) An:Acid = 1 : 1.2   b) An:Acid = 1 : 2   c) An:Acid = 1 : 4

5μm

F: . 6

Fig. 7