

# Protonation and deprotonation behaviour of amine units in polyaniline

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The structures of polyaniline salts chemically synthesized in  $\text{HClO}_4$  of varying concentrations have been examined by means of X-ray photoelectron spectroscopy. The results indicate that, although the imine units of the as-synthesized salt are preferentially protonated, a large proportion of the amine units are also protonated in the presence of a large excess of  $\text{HClO}_4$  on the surface of the salt particles. Protonated amine units are also observed when emeraldine base films cast from *N*-methylpyrrolidinone solutions are reprotonated by  $\text{HClO}_4$ . The deprotonation behaviours of the salt synthesized in  $\text{HClO}_4$ , the reprotonated film and polyaniline from the simultaneous oxidation and polymerization of aniline by  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in acetonitrile are compared. It is found that the protonated amine units undergo deprotonation in aqueous media more readily than the protonated imine units and that both types of structures are stable when heated to  $150^\circ\text{C}$  in air.

(Keywords: polyaniline; amine; protonation; X-ray photoelectron spectroscopy; conducting polymers)

## INTRODUCTION

Electrically conductive polyaniline is most frequently prepared by the oxidative polymerization of aniline by  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in  $\text{HCl}^{1,2}$  to yield emeraldine hydrochloride (EM-HCl). EM-HCl can be converted to the insulating state, EM base, by treatment with  $\text{NH}_4\text{OH}$ . The EM base corresponds to the 50% oxidized poly(*p*-phenyleneamineimine),  $(-\text{C}_6\text{H}_4-\text{NH}-\text{C}_6\text{H}_4-\text{NH}-\text{C}_6\text{H}_4-\text{N}=\text{C}_6\text{H}_4=\text{N}-)_x$ . One of the most important characteristics of polyaniline is the reversible nature of the conductor-to-insulator transition, since the treatment of EM base with excess acid results in the conducting state. From titration studies<sup>3</sup> and theoretical modelling<sup>4</sup>, it has been proposed that the protonation of EM base by  $\text{HCl}$  occurs preferentially at the imine repeat units.

The preferential protonation of imine units in EM-HCl has been confirmed by X-ray photoelectron spectroscopy (x.p.s.) studies<sup>5,6</sup>. In as-synthesized EM-HCl and EM base reprotonated by  $\text{HCl}$ , the N 1s core-level spectrum exhibits a main peak with a binding energy (*BE*) of  $399.4 \pm 0.1$  eV attributable to the amine nitrogens<sup>5-8</sup> and a high *BE* tail above 401 eV, whereas deprotonation of the EM salt results in the disappearance of the high *BE* tail and recovery of the imine peak component at  $398.2 \pm 0.1$  eV. In the present study, x.p.s. is used to demonstrate that the protonation of amine nitrogens can also occur in as-synthesized polyaniline when  $\text{HClO}_4$  is used as the protonic acid. The susceptibility of the protonated amine units to deprotonation is also investigated.

## EXPERIMENTAL

The chemical polymerization of aniline was carried out at  $0-5^\circ\text{C}$  ( $10^\circ\text{C}$  in the case of 0.01 M acid) with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  as oxidant, similar to the method described in the literature<sup>1,2</sup> except that  $\text{HClO}_4$  was used instead of  $\text{HCl}$ . The oxidant-to-aniline ratio was 1:1 and the concentration of  $\text{HClO}_4$  varied from 0.01 M to 1.0 M. The reaction mixture was kept under  $\text{N}_2$  and stirred continuously for 5 h. The product was then filtered and washed with either 0.1 M or 0.01 M  $\text{HClO}_4$ . Drying was carried out at room temperature and under reduced pressure. Stepwise deprotonation was carried out by equilibrating the as-synthesized salt in dilute  $\text{HClO}_4$  (0.01 M or 0.001 M) or deionized  $\text{H}_2\text{O}$ . For comparison purposes, stepwise deprotonation experiments were also carried out for polyaniline perchlorate (PAN- $\text{ClO}_4$ ) salt synthesized via the oxidative polymerization of aniline by  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in acetonitrile<sup>9</sup>, and for EM base films reprotonated by  $\text{HClO}_4$  (ref. 10). The thermal stability of the protonated amine and imine groups was investigated by heating the salts in air at  $150^\circ\text{C}$  for 24 h.

The different chemical states of nitrogen and the doping level were studied using x.p.s. These measurements were carried out on a VG Escalab MkII spectrometer using  $\text{MgK}\alpha$  radiation (1253.6 eV). Samples in the form of powder or film were mounted on the standard sample studs by means of double-sided adhesive tape. All measurements were made with a take-off angle of  $75^\circ$ . The core-level spectra were referenced to the C 1s neutral carbon peak defined at 284.6 eV to compensate for surface charging. The peak width (full width at half-maximum, f.w.h.m.) was maintained constant for all components in a particular spectrum during deconvolution. The

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peak-area ratios for various elements were corrected by experimentally determined instrumental sensitivity factors.

## RESULTS AND DISCUSSION

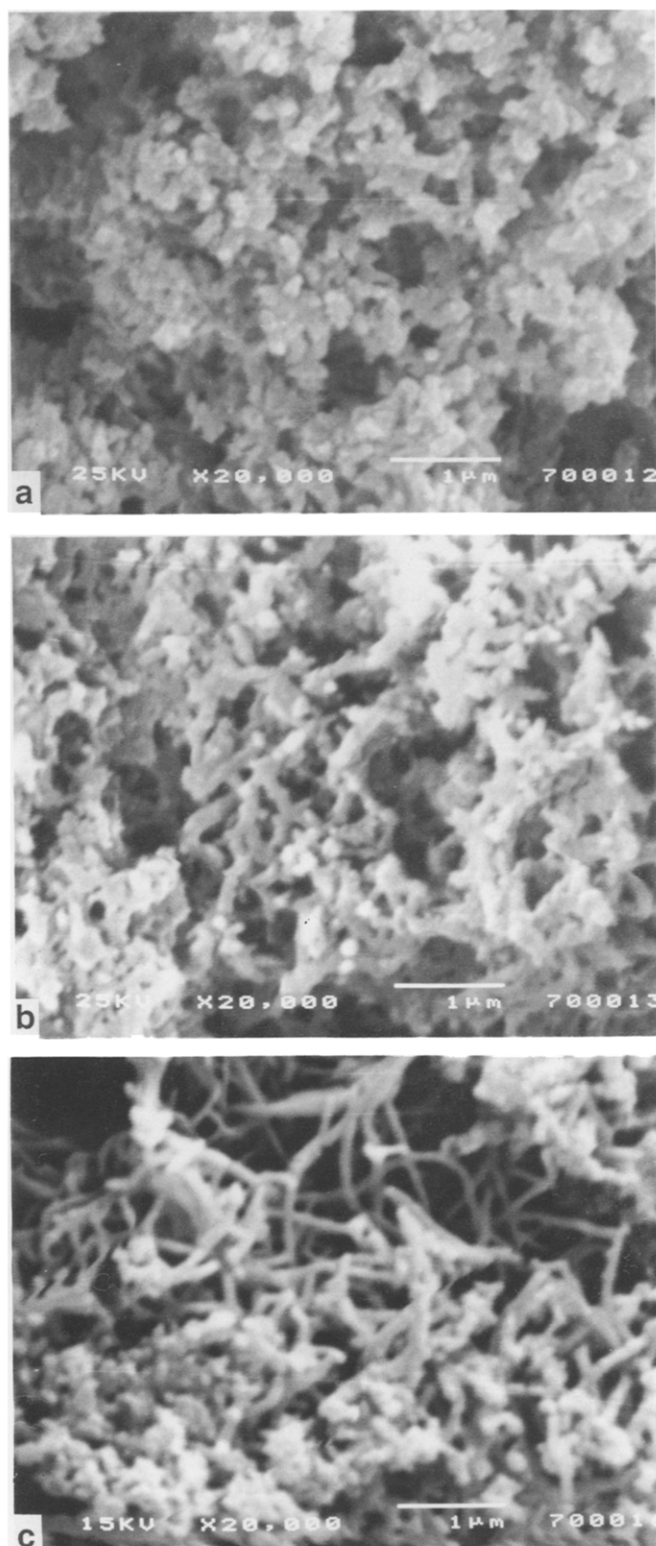
### As-synthesized salts

In the synthesis of EM-HClO<sub>4</sub> in HClO<sub>4</sub> of varying concentrations, different colour changes in the reaction mixture were observed. The yield and colour of the solid product were also different. The synthesis conditions and the product-to-monomer ratios (by weight) obtained are summarized in *Table 1*. A visual comparison of the EM-HClO<sub>4</sub> salt synthesized in 1 M HClO<sub>4</sub> (sample 2 in *Table 1*) with an EM-HCl salt synthesized in 1 M HCl (sample 1) shows the former to be substantially less dense and exhibits solubility in *N*-methylpyrrolidone (NMP). The scanning electron micrographs of samples 1, 2 and 4 (*Figure 1*) clearly show the differences in the morphology of the samples. The polyaniline prepared in 1 M HCl has a more granular texture (*Figure 1a*), somewhat similar to polyaniline electrochemically prepared in HCl<sup>11</sup>. In contrast, the polyaniline samples prepared in HClO<sub>4</sub>, especially at lower concentration (*Figure 1c*), possess a distinct fibrillar structure. This type of morphology has also been reported for polyaniline electrochemically prepared in HBF<sub>4</sub> (ref. 11) and HClO<sub>4</sub> (ref. 12).

The N 1s x.p.s. core-level spectra of the EM-HClO<sub>4</sub> salts are compared with that of the EM-HCl in *Figure 2*. As reported earlier<sup>5</sup>, the core-level N 1s spectrum of the EM-HCl salt (*Figure 2a*) exhibits a predominant amine component peak at 399.4 ± 0.1 eV, a small imine component peak at 398.2 ± 0.1 eV and a high *BE* tail above 401 eV attributable to positively charged nitrogens (N<sup>+</sup>). Based on the fixed f.w.h.m. approach in peak synthesis used in the present work, the high *BE* tail has been resolved as two peaks separated by about 1.5 and 3 eV from the amine peak respectively. These two peaks have been attributed to the polaron-type and bipolaron-type structures<sup>8</sup>, although it is also probable that the N<sup>+</sup> species have a continuous *BE* distribution as a result of charge non-uniformity. The N 1s core-level spectra of the EM-HClO<sub>4</sub> salts (*Figures 2b–d*) indicate that the relative intensities of the N<sup>+</sup> component peaks as well as their *BE*s are highly dependent on the HClO<sub>4</sub> concentration used in the synthesis. When 1 M HClO<sub>4</sub> is used (*Figure 2b*), the second (higher *BE*) N<sup>+</sup> component peak is the predominant peak and the *BE* separation between this peak and the amine peak is 2.4 eV. As the concentration of the HClO<sub>4</sub> is decreased, the protonation level as given by the N<sup>+</sup>/N ratio also decreases as expected. However, the intensity of the first N<sup>+</sup> component peak increases relative to the second N<sup>+</sup> component peak and the *BE* separation between these two peaks increases. The N 1s core-level spectrum in *Figure 2d* shows the N<sup>+</sup> species to be distributed in a manner similar to that of the EM-HCl salt (*Figure 2a*).

**Table 1** Synthesis conditions and product yield of polyaniline samples

Sample	Synthesis medium	Washing agent	Wt product Wt monomer
1	1 M HCl	0.1 M HCl	0.77
2	1 M HClO <sub>4</sub>	0.1 M HClO <sub>4</sub>	0.92
3	0.1 M HClO <sub>4</sub>	0.1 M HClO <sub>4</sub>	0.80
4	0.01 M HClO <sub>4</sub>	0.01 M HClO <sub>4</sub>	0.47



**Figure 1** Scanning electron micrographs of polyaniline prepared in (a) 1 M HCl (sample 1), (b) 1 M HClO<sub>4</sub> (sample 2) and (c) 0.01 M HClO<sub>4</sub> (sample 4)

However, the actual protonation level in the EM-HCl salt may be higher than that indicated by the x.p.s. data owing to the possible loss of the volatile acid in the high-vacuum environment during x.p.s. measurements.

The anion/N ratios of the EM-HCl and EM-HClO<sub>4</sub> salts are calculated from the ratios of the peak areas of the appropriate components in the Cl 2p and N 1s spectra with correction using the sensitivity factors. The Cl 2p

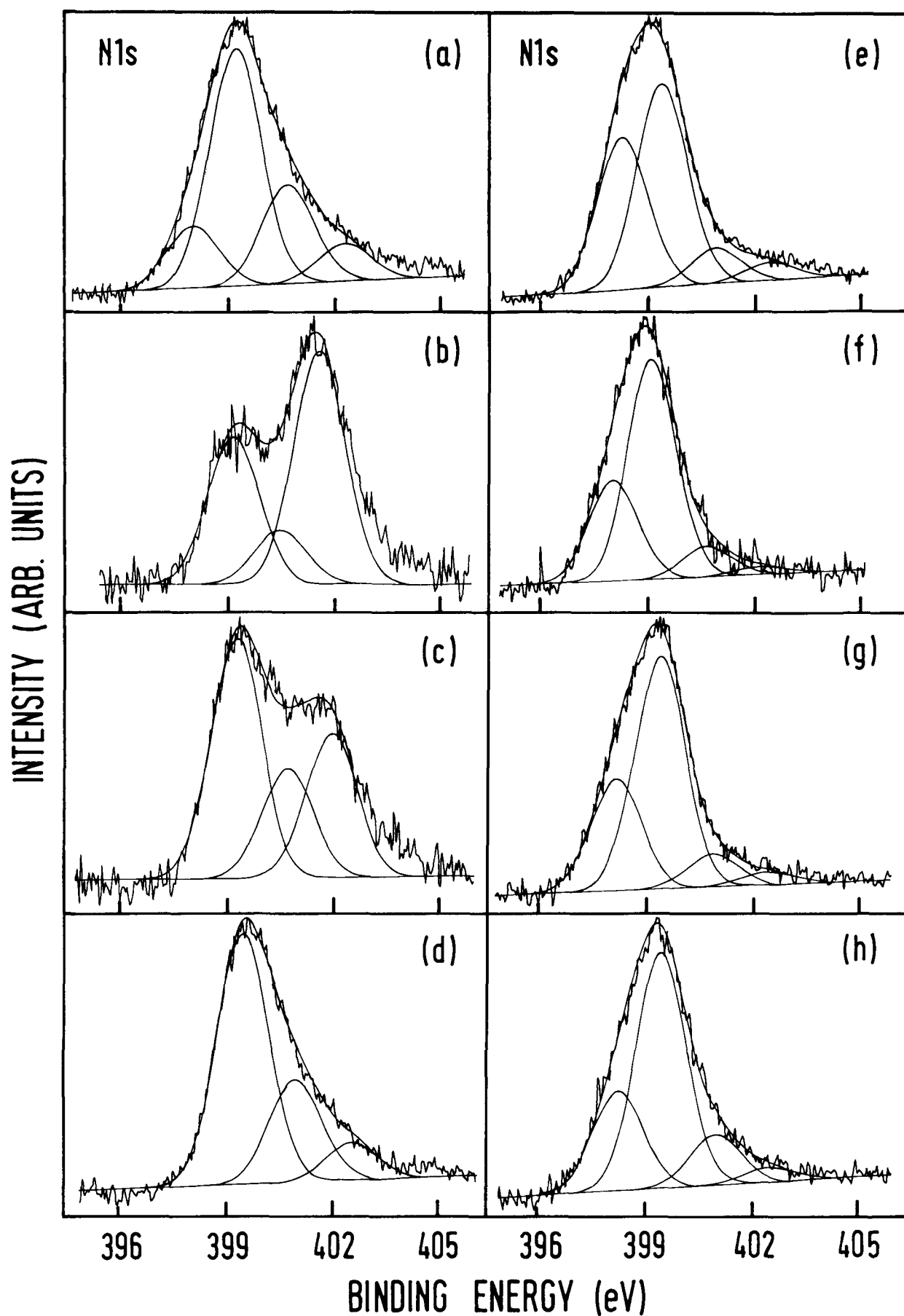


Figure 2 N 1s core-level spectra of (a) sample 1, (b) sample 2, (c) sample 3, (d) sample 4; (e), (f), (g) and (h) samples 1, 2, 3 and 4, respectively, after treatment with 0.5 M NaOH

core-level spectrum of the EM-HCl salt has been resolved into three spin-orbit doublets (Cl 2p<sub>1/2</sub> and Cl 2p<sub>3/2</sub>) with the BEs for the Cl 2p<sub>3/2</sub> peaks lying at 197.1, 198.6 and 200.1 eV<sup>13</sup>. The Cl 2p components at 197.1 and 200.1 eV are attributable to the ionic (Cl<sup>-</sup>) and covalent (-Cl) species respectively<sup>5</sup>. The chlorine species with the intermediate BE of 198.6 eV (Cl\*) probably arises from charge interaction between the chlorine dopant and the highly conductive polymer chain, and has been reported for HCl-protonated polyaniline<sup>14</sup> and polypyrrole chloride complexes<sup>13</sup>. The Cl 2p core-level spectra of the EM-HClO<sub>4</sub> salts indicate two envelopes at 199 and 207 eV. The higher BE envelope is assigned to the ClO<sub>4</sub><sup>-</sup> anion<sup>15</sup>. The X-ray satellite lines from the peak in the 207 eV region as well as the presence of chlorine (Cl<sup>-</sup>, -Cl) species will contribute to the envelope in the 199 eV region, which is of much lower intensity than the former peak. The anion/N and N<sup>+</sup>/N ratios of samples 1 to 4 are compared in Table 2. The use of a non-volatile acid such as HClO<sub>4</sub> in the synthesis of polyaniline invariably results in some adsorbed acid on the polymer surface upon drying *in vacuo*. As a result the ClO<sub>4</sub><sup>-</sup>/N ratio can be substantially higher than the N<sup>+</sup>/N ratio when HClO<sub>4</sub> of higher concentration is used (sample 2).

The N 1s core-level spectra of base samples obtained from the deprotonation of samples 2 to 4 are rather similar (Figures 2f-h) even though the intermediate products and rate of polymerization are affected by the concentration of the HClO<sub>4</sub>. The intrinsic oxidation state (as indicated by the distribution of the imine and amine units) of these samples is lower than that of the base of EM-HCl (Figure 2e). In all these base samples, the residual high BE tail in the N 1s spectra accounts for about 10–15% of the total nitrogen. Since no ionic chlorine (ClO<sub>4</sub><sup>-</sup> or Cl<sup>-</sup>) is detected in these base samples, the residual high BE tail is attributed to surface oxidation products. The distributions of the N species of the bases are tabulated in Table 2. A comparison of the N 1s core-level spectra of the EM-HClO<sub>4</sub> salts and bases indicates that a large proportion of the amine units in the as-synthesized salts are protonated in the presence of HClO<sub>4</sub> of high concentration. Although the intensity of the higher BE N<sup>+</sup> component peak increases relative to the lower BE N<sup>+</sup> component as more amine units are protonated, it would not be correct to assign the former to protonated amine (-N<sup>+</sup>H<sub>2</sub>-) and the latter to protonated imine species (=N<sup>+</sup>H-). This can be illustrated by the case of sample 2, where about half of the amine units (comparing -NH-/N ratios of the salt and base) and all the imine units are protonated. The numbers of protonated imine and amine units are therefore

comparable but the higher BE N<sup>+</sup> component is more than four times more intense than the first N<sup>+</sup> component. It has been proposed that the protonation of the imine units of EM base results in the N atoms existing as semiquinone moieties, which give rise to the polaron band<sup>2,4</sup>. It is likely that the presence of a substantial number of protonated amine groups will interfere with the formation of the polaron band. The x.p.s. data suggest that, with increasing number of protonated amine units, a large proportion of the N<sup>+</sup> atoms become uniformly charged and in a more positive environment than when only protonated imine units are predominant.

#### Partial deprotonation and reprotonation

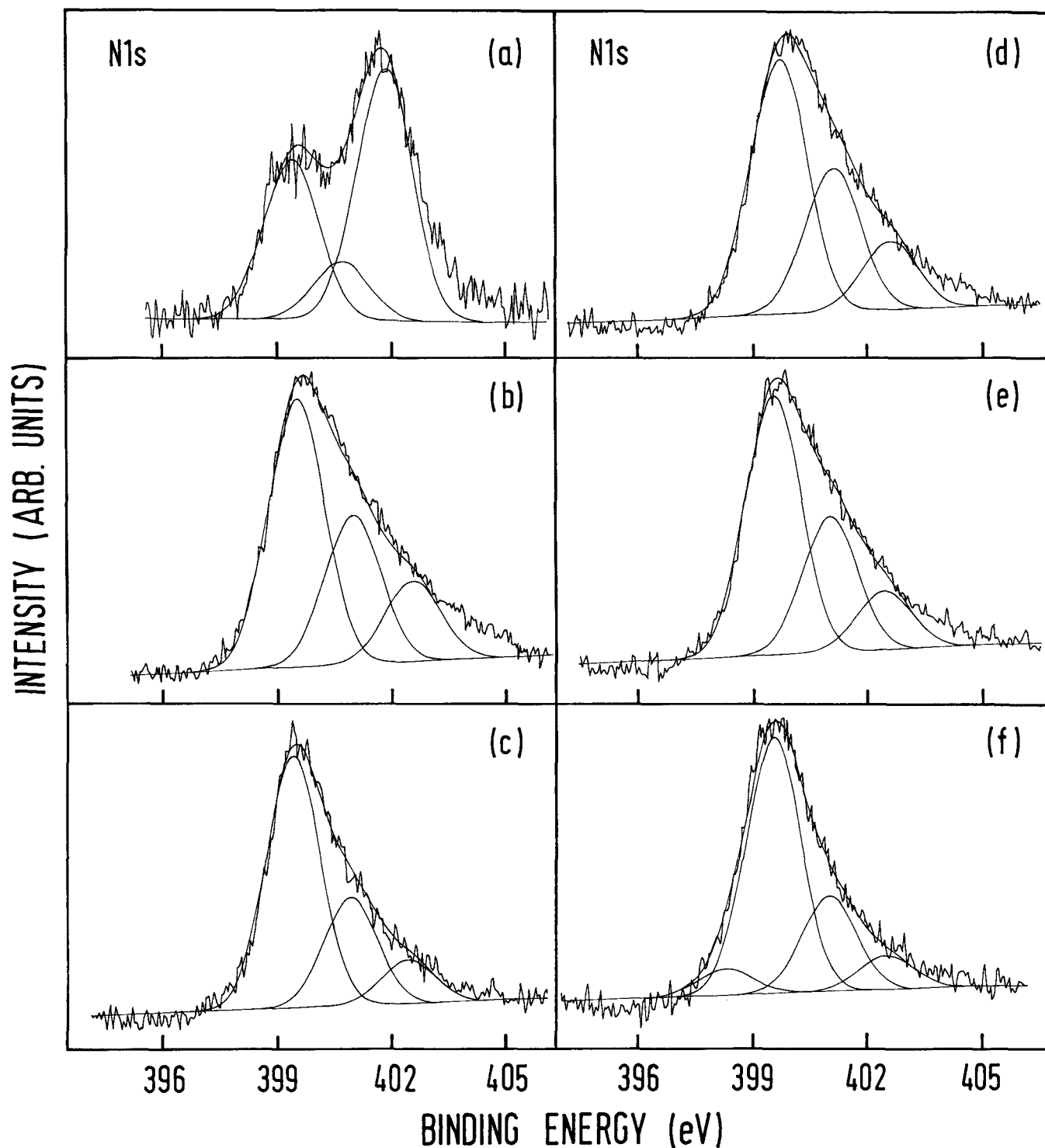
The higher susceptibility of the protonated amine units to deprotonation as compared to the protonated imine units is illustrated by the N 1s core-level spectra obtained from the progressive partial deprotonation of sample 2, as shown in Figure 3. (For ease of comparison, Figure 2b is reproduced as Figure 3a.) After sample 2 is equilibrated with 0.01 M HClO<sub>4</sub>, the N 1s core-level spectrum (Figure 3b) shows the polymer to be 46% protonated and the distribution of charges on the N<sup>+</sup> species is such that the two N<sup>+</sup> component peaks are 1.5 and 3 eV from the amine peak (similar to samples 1 and 4). A higher extent of deprotonation is achieved with H<sub>2</sub>O, with the recovery of the neutral amine units to the same level as in the base (Figure 3c). However, the absence of an imine component peak in the N 1s core-level spectrum implies that the imine units remained protonated and the high BE tail can similarly be deconvoluted into two component peaks located at 1.5 and 3 eV from the amine peak. This deprotonation behaviour can be compared with that of the polyaniline perchlorate (PAN-ClO<sub>4</sub>) complex obtained from the simultaneous oxidation and polymerization of aniline by copper perchlorate in acetonitrile<sup>9</sup>. The x.p.s. core-level spectra of the as-synthesized salt (Figure 3d, -NH-/N=0.54, N<sup>+</sup>/N=0.46, ClO<sub>4</sub><sup>-</sup>/N=0.53) and the base (-N=/N=0.39, -NH-/N=0.51, N<sup>+</sup>/N=0.10) indicate that the N<sup>+</sup> species in the former are mainly from protonated imine units. In the deconvolution of the N 1s core-level spectra of the PAN-ClO<sub>4</sub> salt and base, the imine and amine peaks are also at 398.2 ± 0.1 eV and 399.4 ± 0.1 eV respectively while the high BE tail is again deconvoluted as two N<sup>+</sup> component peaks as in sample 1. Despite the different nature of the N<sup>+</sup> species in the two as-synthesized perchlorate-doped polyaniline salts, the N<sup>+</sup>/N ratios of both samples after equilibrating in 0.01 M HClO<sub>4</sub> and H<sub>2</sub>O are comparable (comparing Figures 3b and 3e, Figures 3c and 3f). For the PAN-ClO<sub>4</sub>

**Table 2** X.p.s. results of as-synthesized EM-HCl and EM-HClO<sub>4</sub> salts and their bases

Sample	Polymer salt				Base polymer		
	-N=/N <sup>a</sup>	-NH-/N	N <sup>+</sup> /N	Anion/N <sup>b</sup>	-N=/N	-NH-/N	N <sup>+</sup> /N
1	0.14	0.55	0.31	0.29	0.37	0.50	0.13
2	-	0.34	0.66	0.86	0.28	0.61	0.11
3	-	0.49	0.51	0.59	0.29	0.60	0.11
4	-	0.64	0.36	0.26	0.25	0.60	0.15

<sup>a</sup> Neutral imine structure

<sup>b</sup> Based on the corrected chlorine-to-nitrogen core-level spectral area ratios

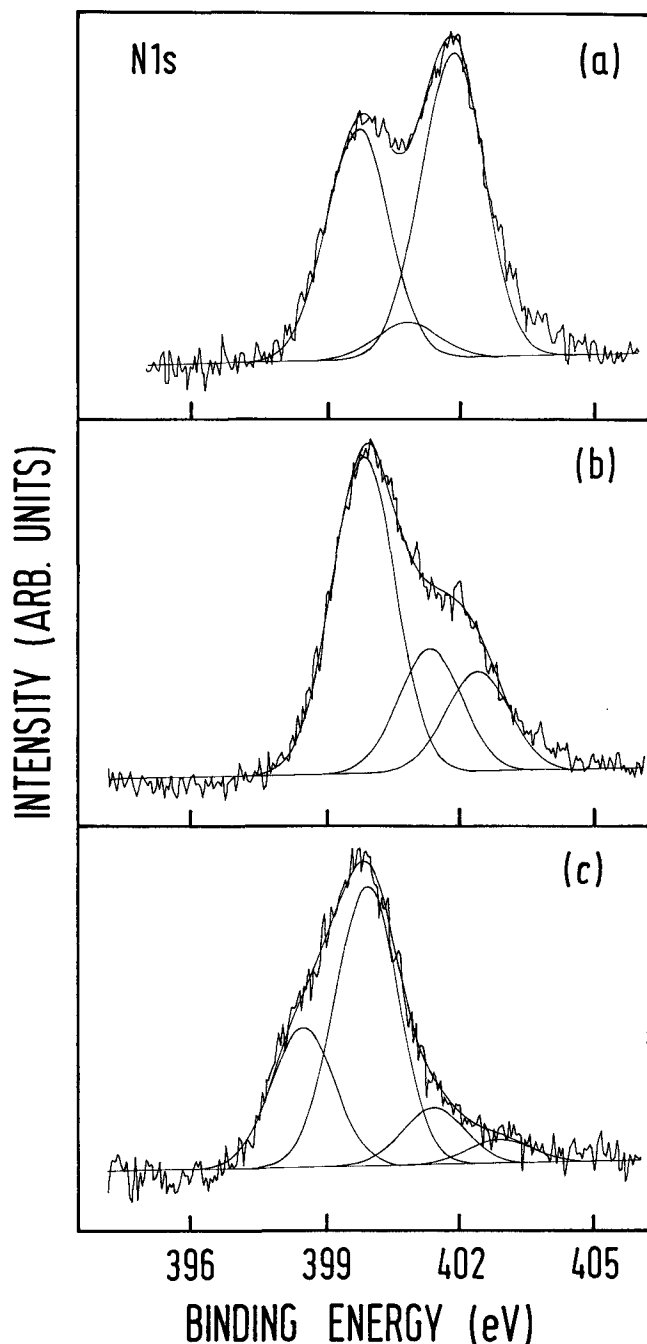


**Figure 3** N 1s core-level spectra of (a) as-synthesized EM-HClO<sub>4</sub> salt (sample 2) and the salt after equilibrating in (b) 0.01 M HClO<sub>4</sub> and (c) deionized H<sub>2</sub>O, and (d) as-synthesized PAN-ClO<sub>4</sub> salt from Cu(ClO<sub>4</sub>)<sub>2</sub> and the salt after equilibrating in (e) 0.01 M HClO<sub>4</sub> and (f) deionized H<sub>2</sub>O

salt, no significant deprotonation occurs when it is equilibrated in 0.01 M HClO<sub>4</sub>. However, a small imine peak is observed when H<sub>2</sub>O is used (Figure 3f). The data suggest that the stability of the protonated imine units in 0.01 M HClO<sub>4</sub> or H<sub>2</sub>O is independent of the state of the amine units (protonated or otherwise). Figure 3 also clearly shows that, upon deprotonation of -N<sup>+</sup>H<sub>2</sub>- units in EM-HClO<sub>4</sub> salt, the charges on the remaining N<sup>+</sup> species are redistributed in a manner similar to that obtained in PAN-ClO<sub>4</sub> salt.

The reprotonation of the base of sample 1 by

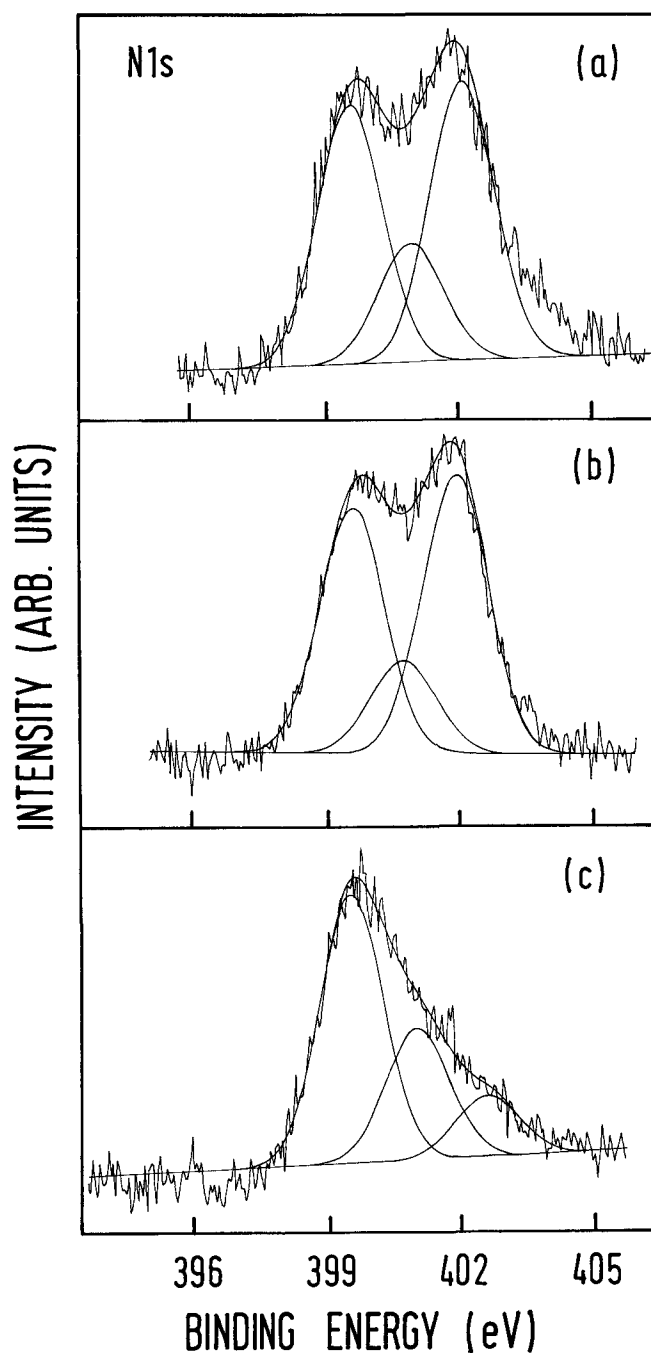
1 M HClO<sub>4</sub> results in a salt possessing -NH-/N, N<sup>+</sup>/N and ClO<sub>4</sub><sup>-</sup>/N ratios of 0.52, 0.48, and 0.86 respectively. The BE separation between the N<sup>+</sup> component peaks is similar to that in the pristine sample 1 salt. The close agreement between the -NH-/N ratios of the sample 1 base and reprotonated salt indicates that the amine units remain substantially unprotonated even though excess HClO<sub>4</sub> is present. A similar outcome is observed even when the concentration of the HClO<sub>4</sub> used in the reprotonation process is increased to 3 M. Thus, the susceptibility of the amine units to



**Figure 4** N 1s core-level spectra of (a) EM base film (from sample 1) after re-protonation by 3 M HClO<sub>4</sub> and the re-protonated film after treatment with (b) 0.1 M HClO<sub>4</sub> and (c) deionized H<sub>2</sub>O

protonation is much higher during the synthesis of the polyaniline in HClO<sub>4</sub> than when the polyaniline base is equilibrated with HClO<sub>4</sub>. However, as reported earlier<sup>10</sup>, EM base films cast from NMP solution show different re-protonation behaviour from the corresponding base powder. The use of 3 M HClO<sub>4</sub> in the re-protonation process readily results in the protonation of the amine units (Figure 4a). However, for such films, structural modifications resulting in a higher intrinsic oxidation state and reduction in solubility are apparent after one re-protonation/deprotonation cycle<sup>10,16</sup>. The N 1s core-level spectra obtained after progressive deprotonation of the 3 M HClO<sub>4</sub> re-protonated salt film are shown in Figures 4b and 4c. The preferential deprotonation of the  $-N^+H_2-$  groups as compared to the  $=N^+H-$  groups

is again observed (comparing Figures 4a and 4b). A large proportion of the imine units are recovered when the re-protonated film is treated with H<sub>2</sub>O (Figure 4c). In this case, the BE separation between the imine and amine component peaks in the N 1s core-level spectrum has increased to 1.4 eV compared to 1.2 eV in the pristine base powder and film. If 0.5 M NaOH is used for complete deprotonation of the salt film, this BE separation further increases to 1.5 eV<sup>10</sup>. This increase in BE separation upon deprotonation of EM salt films is unique to films cast from NMP solutions since EM base powder can be subjected to re-protonation/deprotonation cycles without the N 1s core-level spectra showing any significant deviations from that of the pristine base powder.



**Figure 5** N 1s core-level spectra of (a) sample 2, (b) 3 M HClO<sub>4</sub> re-protonated EM film and (c) PAN-ClO<sub>4</sub> salt from Cu(ClO<sub>4</sub>)<sub>2</sub>, after heat treatment in air at 150°C for 24 h

In contrast to the high susceptibility of the amine units to deprotonation in aqueous media of pH greater than 1, both the protonated amine and imine units are rather stable under heating at 150°C. The N 1s core-level spectra of sample 2 and the 3 M HClO<sub>4</sub> reprotonated salt film after heating in air at 150°C for 24 h (Figures 5a and 5b, respectively) show that the amine content increases by about 10% in the former but remains constant in the latter. In both cases, there is some redistribution of charges on the N<sup>+</sup> species as evidenced by the increase in the intensity of the first N<sup>+</sup> component peak and a corresponding decrease in the second N<sup>+</sup> component peak. However, the BE separation between these two peaks does not change substantially. For the PAN-ClO<sub>4</sub> salt, where the N<sup>+</sup> species are from the protonation of the imine units, the N 1s core-level spectrum of the salt after a similar heat treatment (Figure 5c) also indicates no substantial changes from the pristine spectrum (Figure 3d).

### CONCLUSIONS

The oxidative polymerization of aniline by (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in HClO<sub>4</sub> has been investigated. The as-synthesized salt (EM-HClO<sub>4</sub>) possesses a different morphology than the salt obtained with HCl. X.p.s. results indicate that, in the presence of excess HClO<sub>4</sub> on the surface of the as-synthesized salt, a large proportion of the amine nitrogens can be protonated. Although the protonation level of the salt is strongly dependent on the HClO<sub>4</sub> concentration, the intrinsic oxidation state of the polymer shows no significant variation in the concentration range (0.01 M to 1.0 M) tested. The protonated amine units in the as-synthesized salt and reprotonated salt films are more susceptible to deprotonation in aqueous media than the protonated imine units. However, both the

protonated imine and amine units are stable in air up to 150°C.

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