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Significance of redistribution reactions detected by in situ atomic force microscopy during early stages of fast scan rate redox cycling experiments at a solid 7,7,8,8-tetracyanoquinodimethane-glassy carbon electrode-aqueous (electrolyte) interface

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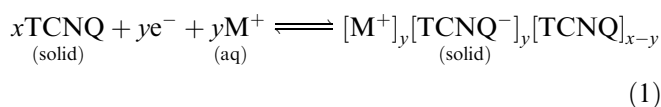
Abstract The reduction of solid 7,7,8,8-tetracyanoquinodimethane (TCNQ) at an electrode-TCNQ-aqueous (electrolyte) is complex, irrespective of whether the solid on the electrode surface is attached by direct adherence or formed by electrochemical deposition. In order to understand the origin of reaction pathways that accompany the $[\text{TCNQ}]^{0/-}$ process, fast scan rate (0.1 V s^{-1}) redox cycling and potential step experiments on TCNQ mechanically attached to a glassy carbon electrode placed in aqueous solution containing 0.1 M electrolyte (KCl, CsCl, or Et_4NCl) have been monitored by the technique of in situ atomic force microscopy (AFM). The shapes of cycling voltammograms are consistent with the presence of a mixture of diffusion and surface processes in the initial cycles. AFM results show that, during the early stage of the redox cycling experiments, electrochemical reduction of TCNQ to sparingly soluble TCNQ^- is accompanied by a redistribution process. This rearrangement results in the transformation of arrays of almost amorphous solid to a lower energy microcrystalline state which has a more thin film-type appearance. When CsCl is the electrolyte, long needle-type crystals are detected by the AFM method after long periods of redox cycling. The identity of the cation in the supporting electrolyte and the solubility of the reduced salt formed by reduction of TCNQ affect the nature of the voltammetry observed during early stages of redox cycling. When the redistribution process is completed and the stable crystalline phase is formed, the voltammetry of the $[\text{TCNQ}]^{0/-}$ couple is

predominantly controlled by a nucleation-growth mechanism.

Key words 7,7,8,8-Tetracyanoquinodimethane · Atomic force microscopy · Redistribution reaction · Redox cycling

Introduction

TCNQ (7,7,8,8-tetracyanoquinodimethane) is significantly conducting and the remarkable electrical properties of some of the solid TCNQ salts [1, 2] have enabled them to be used as electrodes [3–6], potentiometric sensors [7, 8], high-density molecular-based information storage media [9] and in electrochromic devices [10]. Thus, not surprisingly, solid TCNQ and its reduced salts have been subjected to extensive electrochemical studies [1]. In early studies by Jaeger and Bard [3, 4], electrodes prepared as compacted pellets from conductive donor-acceptor complexes of TCNQ with several donors were investigated in aqueous media containing metal ion salts in the electrolyte. It has been reported that upon exceeding the potential limits of stability of the electrode, the electrode is reduced or oxidized leading to the decomposition of the electrode and the formation of an insoluble compound on the electrode surface [1, 3, 4]. These insoluble compounds can be detected by cyclic voltammetry, which shows symmetrical peaks attributable to the reduction of insoluble TCNQ and the oxidation of the insoluble TCNQ^- metal salts according to Eq. 1:



Recently, Chambers et al. [11–13] claimed that the cyclic voltammetry of a $[\text{TCNQ}]^{0/-}$ couple generated from thin polycrystalline films of [9-aminoacridinium (TCNQ_2)] in contact with 1.0 M potassium acetate does not corres-

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pond to a simple electron-transfer reaction of surface-confined species. All the voltammograms of the solid $[\text{TCNQ}]^{0/-}$ couple in contact with different electrolytes are characterized by narrow peak widths much less than $3.52 RT/F$ for a one-electron process, wide hysteresis (> 200 mV) between the anodic and cathodic peaks, and significant double layer capacities [1, 11, 12, 14–16]. Chambers et al. [11, 14] claim that the 3D instantaneous nucleation model describes very well the characteristics observed in the cyclic voltammetry of the $[\text{TCNQ}]^{0/-}$ couple. Bond et al. [15, 17] have also recently extended their studies of the mechanism and, like other authors [1, 5, 11, 14], concluded that the process is associated with many equivalent monolayers of surface-attached material.

Figure 1 illustrates the nature of the voltammetry according to a nucleation-growth mechanism that has attracted most of the attention [1, 11, 14–17]. However, Chambers et al. [11, 14] only interpreted data obtained at low sweep rates and low coverages because of the diffusion tails that are evident at other conditions. Bond et al. [16] prevented the loss of material from the surface by addition of a Nafion coating and the data were evaluated after extensive redox cycling of the potential when the voltammograms had developed the shape observed in Fig. 1. The initial stages of redox cycling do not generate reproducible voltammograms resembling Fig. 1; the shapes change and the peak heights decrease during the first few cycles until after about 10 cycles, when a stable response characteristic of Fig. 1 is achieved.

Electrochemical quartz crystal microbalance (EQCM) studies of TCNQ conducting salts showed that the initial reduction step after electrogeneration of the TCNQ surface state from [9-aminoacridinium (TCNQ_2)] gave anomalously large frequency transients indicative of extensive hydration or surface structural changes [12]. Several cycles between the oxidized and reduced states were required in order to establish both a chemical reversible voltammetric and EQCM response [12]. In situ

rotating disk electrode and simultaneous electrochemical electron spin resonance (ESR) experiments suggest that a dissolution-reprecipitation process may be associated with the initially unstable voltammetric response and the redistribution of the TCNQ solid on the electrode surface [1, 17]. It is clear that, at fast sweep rates and early experimental times during the course of redox cycling experiments, the voltammetry of the $[\text{TCNQ}]^{0/-}$ couple is not accounted for by the nucleation-growth model [1, 11, 14–16]. After extensive redox cycling of the potential, ex situ electron microscopy and X-ray diffraction studies [15, 16] suggested that a transformation of at least part of the material from an almost amorphous solid (initially immobilized onto the electrode) into a well-defined crystalline material occurred.

Since the electrochemical dissolution process of TTF-TCNQ single-crystal electrodes has been studied by Bartlett and Tong [18] using in situ scanning tunneling microscopy, to date only the ex situ technique of electron scanning microscopy and X-ray diffraction have been used to detect the morphological changes at micrometer and nanometer scales that occur after extensive redox cycling of microcrystals of TCNQ mechanically attached to an electrode surface [15, 16]. In order to characterize the processes that occur during the initial stages of the voltammetry of solid TCNQ, in situ rather than ex situ forms of microscopy are required.

In this present investigation, we have employed the in situ technique of atomic force microscopy (AFM) [19] to monitor the morphological changes that occur on the electrode surface in the initial stages of fast scan rate redox cycling experiments at a TCNQ-glassy carbon-aqueous (electrolyte) interface. Solutions of KCl, CsCl and Et_4NCl were used as electrolyte, so that formation of a range of TCNQ salts of different solubility and containing cations with different sizes and hence crystal morphologies were studied. Via analysis of the AFM data, a definitive understanding of the factors contributing to the pronounced voltammetric and crystal morphology changes that occur at the early stages of redox cycling experiments has been obtained.

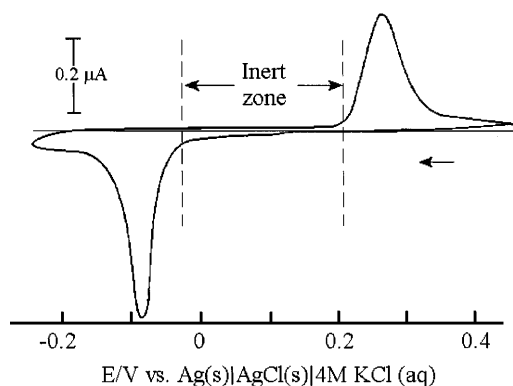


Fig. 1 Schematic diagram of the voltammetric response for the surface-attached $[\text{TCNQ}]^{0/-}$ system when interconversion of TCNQ and the reduced salt occurs by a nucleation-growth mechanism [11, 14–16]

Experimental

A Topometrix TMX 2010 Discoverer atomic force microscope, operating in the contact mode, was employed to image the TCNQ abrasively attached to a glassy carbon electrode (3 mm diameter). The experimental details for the electrochemical AFM cell have been described previously [19]. Pyramidal silicon nitride tips (Topometrix AFM E-Chem probes 1750) were employed. The images were obtained with a resolution of 200×200 data points per image and the scanning rate was about 10 Hz. In all cases, simultaneous recordings of the cyclic voltammograms and conventional AFM topographical images were undertaken. Measurements were made under ambient temperature conditions of 20 ± 2 °C.

The glassy carbon electrode was polished with a succession of diamond lapping compounds (Kemet International, Kent, UK) from 1 μm down to 0.1 μm particle size and then sonicated for 20 min before use. The solid TCNQ was attached to the electrode

surface as follows. First, approximately 5 mg of TCNQ powder was placed on a filter paper (Whatman 1). The electrode was then gently rubbed into the powder until abrasive attachment of TCNQ was evident via visual observation of a shiny yellow colour when the electrode was observed at a low angle. Finally, the electrode was transferred to the AFM electrochemical cell. The electrochemical reaction was carried out in the presence of an aqueous solution containing 0.1 M of the supporting electrolyte (KCl, CsCl or Et₄NCl). The reference electrode was Ag/AgCl (0.1 M electrolyte) and the counter electrode was a platinum wire.

During a typical experiment, an electrode area of between $1 \times 1 \mu\text{m}^2$ and $50 \times 50 \mu\text{m}^2$ was initially imaged at open circuit potential. Subsequently, a potential of 0.4 V or 0.5 V against the Ag/AgCl electrode was applied to the TCNQ modified glassy carbon electrode and then the topographic changes occurring during about 600 s were recorded. These initial experiments enabled the stability of the oxidized form of TCNQ to be established after it had been attached to a glassy carbon electrode. Finally, topographic images of exactly the same area of the electrode were obtained after cycling the potential over the 0.4 V or 0.5 V to -0.2 V versus Ag/AgCl, or during the course of cycling the potential or during potential step experiments. The potential scan rate used in all voltammetric experiments was 0.1 V s^{-1} , which corresponds to the situation when Chambers et al. [11–14] have observed considerable complications and was not considered in their tabulated data.

Aqueous solutions were prepared from triply distilled deionized water obtained from an Elgastat UHQ apparatus (resistivity greater than $10^7 \Omega \text{ cm}$). AnalaR grade reagents KCl, CsCl, CaCl₂ and Et₄NCl hydrate were used as purchased from Aldrich. No attempt was made to remove oxygen during the course of the electrochemical experiments.

Results

Figure 2 shows an AFM image in air of the almost amorphous and weakly diffracting [15, 17] form of TCNQ mechanically attached to a glassy carbon elec-

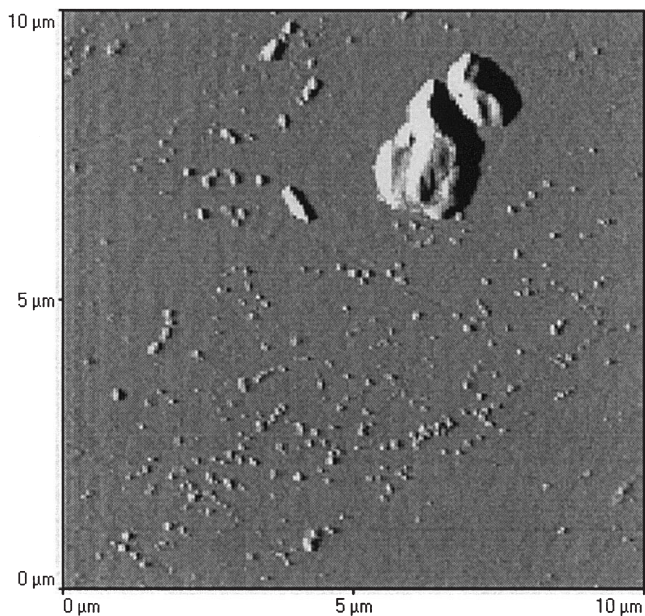


Fig. 2 AFM image obtained in air of almost amorphous (weakly refracting [15, 16]) TCNQ particles attached to a glassy carbon electrode

trode. The range of sizes of the attached solid particles over the area of electrode imaged was between $0.1 \mu\text{m}$ and $1 \mu\text{m}$. The mechanical stability of the particles over the scanning area was tested during continuous scanning, and no movement or loss of material was detected.

In the presence of 0.1 M KCl as supporting electrolyte, ex situ X-ray data [15, 16] reveal that the $[\text{K}^+][\text{TCNQ}^-]$ salt is formed when TCNQ mechanically attached to an electrode surface is reduced. The electrode process occurring during the course of redox cycling can be represented by Eq. 2:

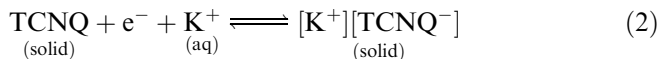
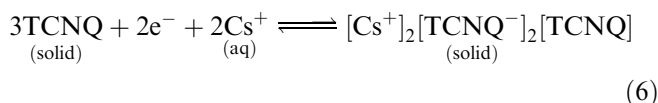


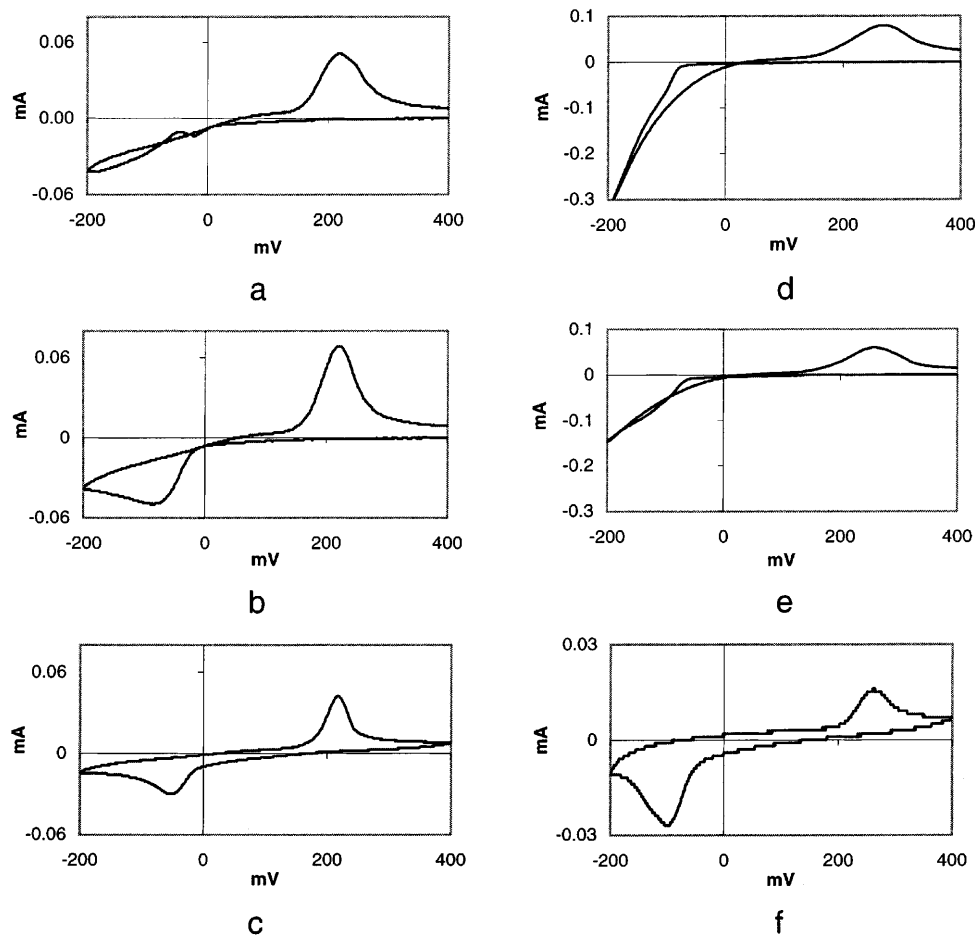
Figure 3a–c contains a series of voltammograms of the $[\text{TCNQ}]^{0/-}$ process in 0.1 M KCl obtained with a scan rate of 0.1 V s^{-1} , using the in situ AFM electrochemical cell, when the potential is scanned at a glassy carbon electrode over the range of $+0.4 \text{ V}$ to -0.2 V versus Ag/AgCl. Clearly, the initial reduction stages produce an extremely complex (and non-reproducible) voltammetric response with current crossover and stochastic of the type attributable to a nucleation-growth mechanism being evident. However, a stable voltammetric response begins to emerge, after approximately five cycles.

Figure 3d–f shows a series of voltammograms obtained during the course of redox cycling of solid TCNQ with 0.1 M CsCl as the electrolyte. Again the initial voltammograms are very complex, but after six cycles the voltammetric response is as expected on the basis of the nucleation-growth mechanism [11, 14–16]. Additional redox cycling leads to a decrease in the magnitude of the current, but the principal features of the voltammogram are retained. X-ray data on the reduced form of the crystal generated in the presence of 0.1 M CsCl indicate that the $[\text{Cs}^+]_2[\text{TCNQ}^-]_2[\text{TCNQ}]$ salt is formed [15, 16]. The redox reaction is



The voltammograms in Fig. 3c and 3f, but not 3a nor 3d, conform to the responses predicted when a solid phase nucleation-growth mechanism occurs, as discussed in the literature [11, 14–16]. That is, after a time of redox cycling a new $[\text{M}^{n+}]_m[\text{TCNQ}^{m-}]_n$ phase initially is generated at the electrode interface when the reduction potential is reached [15, 16]. Concomitant with electron transfer, uptake of M^{n+} ions occurs from the solution phase to allow charge neutralization. It has been shown elsewhere [15, 16] that a significant overpotential is required before nuclei of critical size are formed and enable the rapid growth of a new solid phase. The nucleation-growth mechanism inherently does not require dissolution of a solid phase to occur in order to cause interconversion of TCNQ and its reduced salt. However, voltammetric features evident at the first

Fig. 3 Voltammograms obtained at a scan rate was 0.1 V s^{-1} after almost amorphous TCNQ is mechanically attached to a glassy carbon electrode which then placed in 0.1 M KCl (a, b, c) (a first, b third and c tenth scan, respectively) or in 0.1 M CsCl (d, e, f) (d first, e third and f sixth scan, respectively). The reference electrode was Ag/AgCl (0.1 M electrolyte)



stages of redox cycling at fast scan rate in this study and in the work of Chambers et al. [11, 14] cannot be explained solely on the basis of a solid state nucleation-growth mechanism.

The presence of diffusion in the early stage of the electrochemical reaction is evidenced by the presence of a characteristic “diffusion tail” on the trailing edge of the reduction peak. That is, the current does not rapidly return to the base line current after passing the peak value, as would be expected in a purely solid state reaction. The fact that the onset of diffusional behaviour is more evident in the cathodic than the anodic process is probably related to asymmetry in the electrode reaction with respect to the cation uptake (reduction) and loss (oxidation) [11, 12] and differences in the solubility of the reduced and oxidized forms [20]. Also in the initial voltammograms, a finite current is detected in the “inert region”, which probably is associated with the transient release of soluble TCNQ species into the diffusion layer [17, 18, 21].

AFM images obtained during redox cycling of TCNQ with 0.1 M KCl as the electrolyte are shown in Fig. 4a–c. After two potential cycles between 0.4 V and -0.2 V , the larger sized (weakly diffracting) amorphous particles are clearly transformed to submicron sized particles. Figure 4d–f shows a sequence of AFM images

of TCNQ particles adhered to the electrode surface during redox cycling in 0.1 M CsCl . These results show that the three particles in the centre of the Fig. 4d–f progressively decrease in size while, at the same time, transformed material is evident at the top area of Fig. 4d–f. It is therefore clear that redistribution and dissolution processes are involved in the initial stages of redox cycling experiments. Data in Fig. 4 imply that the electrochemical-induced dissolution reactions are faster when KCl is the electrolyte than in the case with CsCl as the electrolyte.

After 20 potential cycles with 0.1 M CsCl as the electrolyte, needle-like crystals were detected on the electrode surface, as shown in Fig. 5a and 5b. This process apparently represents a second form of redistribution which is not associated with the initial cycling and complex form of cyclic voltammograms. The stability of the crystalline needles during potential step experiments was studied. Figure 5b–d shows an example of a sequence of AFM images in the same area of the crystals at (b) open circuit, (c) at $+0.4 \text{ V}$ and (d) -0.2 V versus Ag/AgCl (0.1 M electrolyte). The images in Fig. 5 are displayed in a shaded form in order to enhance the image details. Apparently, application of a positive potential of 0.4 V destroyed some crystals during the first 30 s and induced fractures in the larger

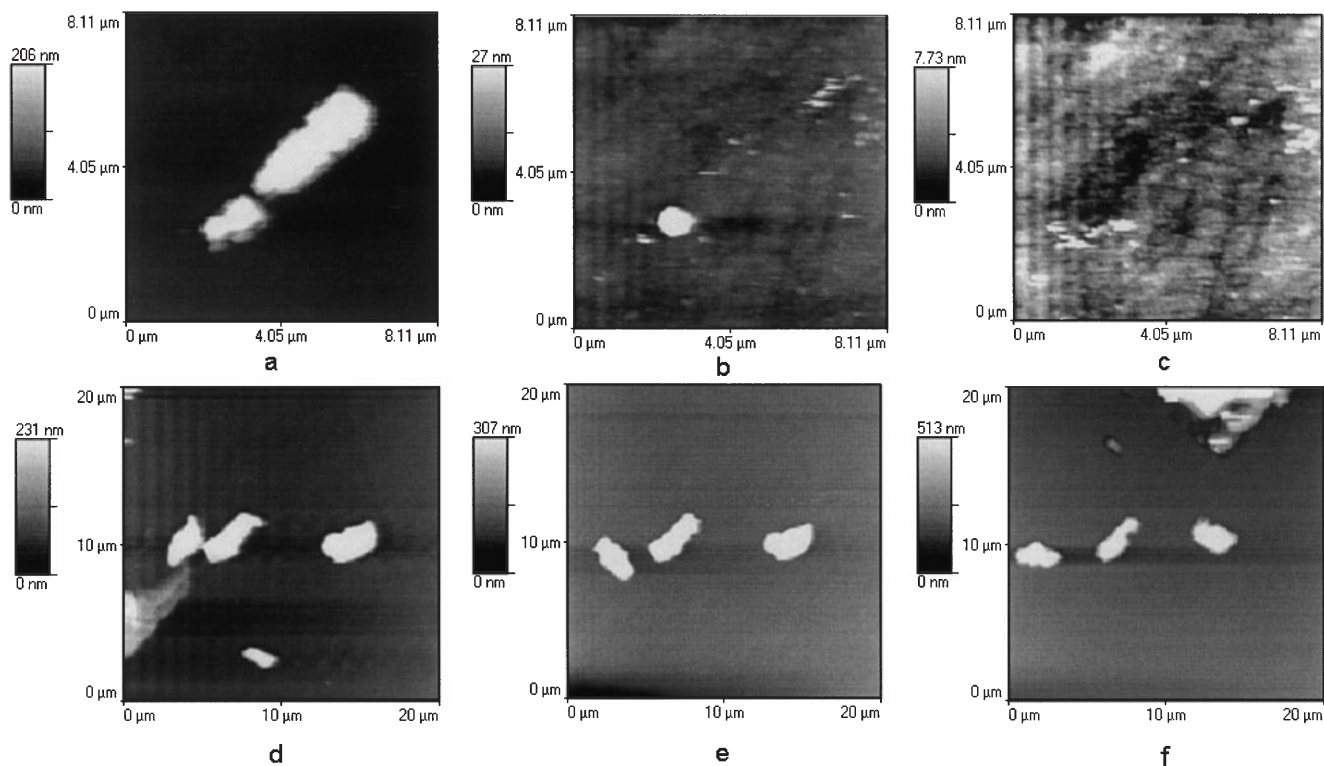


Fig. 4 Sequences of in situ AFM images of the $[\text{TCNQ}]^{0/-}$ system attached to a glassy carbon electrode obtained at 0.4 V when (a, b, c) 0.1 M KCl is the electrolyte (after a 0, b 1 and c 2 potential cycles between 0.4 V and -0.2 V) and when (d, e, f) 0.1 M CsCl is the electrolyte (after d 0, e 2 and f 4 potential cycles between 0.4 V and -0.2 V). The scan rate was 0.1 V s^{-1} and the reference electrode was Ag/AgCl (0.1 M electrolyte)

ones (compare Fig. 5b and 5c). However, no further dissolution or redistribution reactions occurred for a period of 3 min. In contrast, application of a negative potential of -0.2 V destroyed all needle-shaped crystals in a few seconds.

Ex situ electron scanning microscopy [15, 16] after multiple redox cycling and removal of the reduced form of TCNQ from the solution phase also revealed the presence of very long needles when 0.1 M CsCl was used as the electrolyte. The in situ AFM method confirmed these results, but also revealed the presence of a significant contribution to the voltammetry from a redistribution process at early stages during the initial process of redox cycling at fast scan rate.

When 0.1 M Et_4NCl is the electrolyte, significantly different voltammetric data (Fig. 6a–c) were obtained relative to the case when an electrolyte containing a metal cation was used. In this case, no evidence of any diffusion process associated with dissolution of TCNQ or TCNQ^- was detected and the very first scan has the features predicted for a nucleation-growth process. However, a potential shift and a decrease in the peak current was observed on subsequent cycling of the potential. The AFM data revealed that, in the presence of Et_4NCl as electrolyte, the redistribution reaction was

predominantly observed with the smaller particles during the course of voltammetric redox cycling, as shown in Fig. 7a–c. The reactivity-particle size relationship is somewhat random, but data suggest that the probability of a redistribution reaction associated with the smaller sized particles is higher than for the larger sized particles under condition of redox cycling experiments at fast scan rates. The reduction of the separation of the anodic and cathodic peaks during the initial stages of redox cycling is probably due to the slow transformation of the initial amorphous solid phase to a more electroactive solid material. When the potential was maintained at $+0.5$ V, very little changes occurred in the AFM images over very long time periods (of the order of 30 min). In contrast, when the potential was maintained at -0.2 V, the larger particles were eventually redistributed and became smaller in size, but only on the minutes timescale of voltammetry, as shown in Fig. 8. The lack of complex initial cycles associated with the presence of diffusion when Et_4NCl is the electrolyte is attributed the lower solubility of Et_4N^+ salt of TCNQ^- relative to the metal ion salts of TCNQ^- [3, 4].

A detailed examination of the electrode surface with more resolution AFM conditions revealed that, in all cases, almost amorphous TCNQ particles of submicron size were transformed into a thin layer of material during the course of the redox cycling. The structure of this thin layer of material depends of the electrolyte used, as shown in Fig. 9. When KCl is used as electrolyte, a very regular surface coverage develops over the electrode (“bricks in a wall” model). In contrast, when CsCl is the electrolyte a different dendritic shape morphology was

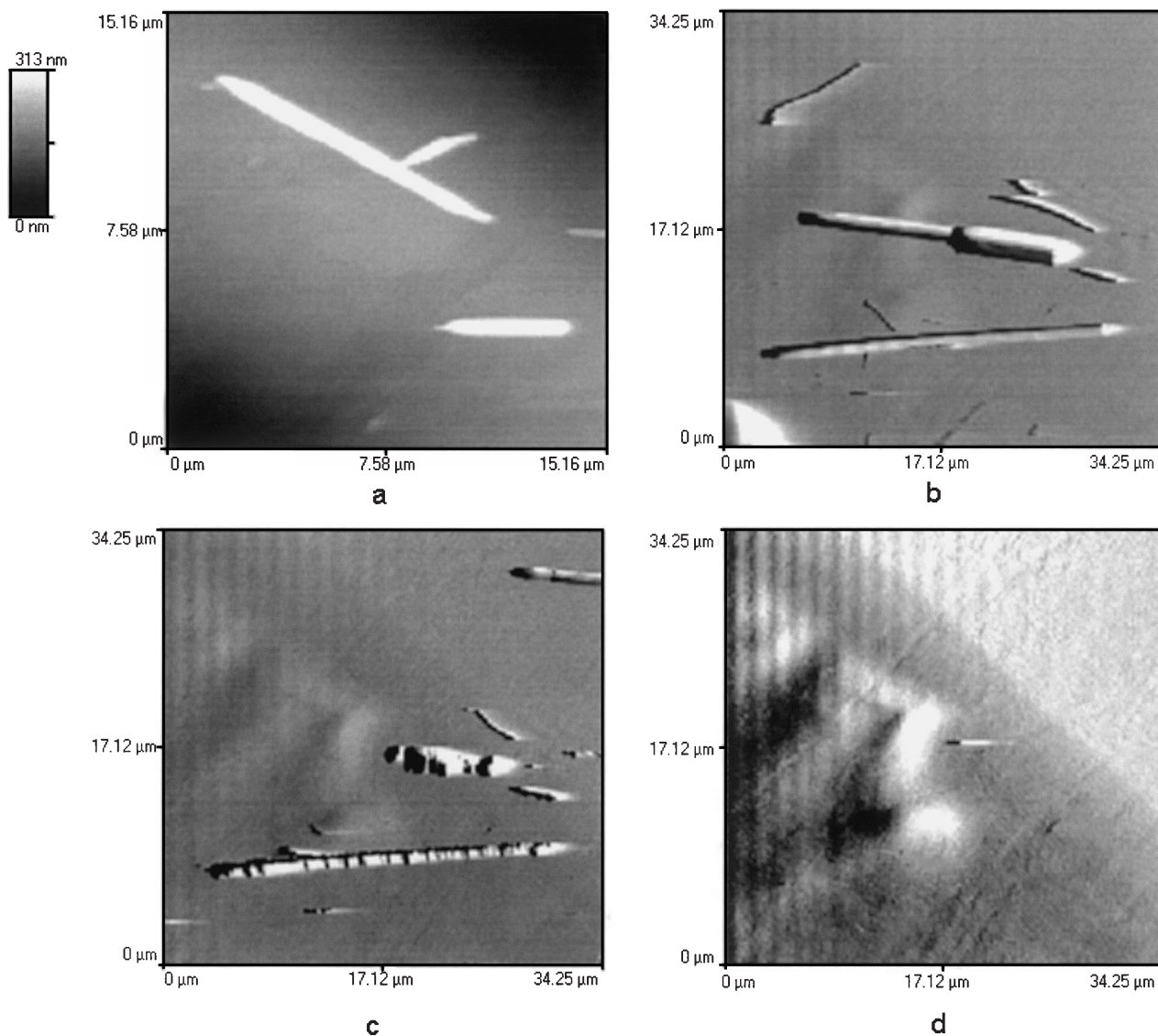


Fig. 5a-d In situ AFM images of the $[\text{TCNQ}]^{0-}$ system attached to a glassy carbon electrode obtained after 20 potential cycles at a scan rate of 0.1 V s^{-1} between 0.4 V and -0.2 V with 0.1 M CsCl as the electrolyte. **a** Topographic AFM image at open circuit potential of the needle-like crystals formed after redox cycling; **b, c, d** sequence of shaded AFM images obtained at **b** open circuit potential, **c** at $+0.4 \text{ V}$ and **d** at -0.2 V . The roughness of the images are approximately $2 \mu\text{m}$ for **b** and **c**, and $0.6 \mu\text{m}$ for **d**. The reference electrode was Ag/AgCl (0.1 M electrolyte)

observed. Apparently, during redox cycling on a glassy carbon electrode the initially energetically unstable solid almost amorphous phase of TCNQ is transformed into at least two more energetically stable solid phases; initially a solid thin layer is formed from which the crystalline form with a needle-like shape is evolved when 0.1 M CsCl is the electrolyte. Needle-shaped crystals have been detected with other electrolytes when TCNQ is attached to a gold electrode [15, 16], so that the crystal growth stage appears to be a function of the electrode substrate.

Discussion

The simultaneous voltammetry-in situ AFM experiments undertaken in this study at a scan rate of 0.1 V s^{-1} demonstrate that a redistribution reaction makes a significant contribution to the early stages of fast scan rate voltammetric redox cycling experiments involving the chemically reversible conversion of mechanically attached TCNQ to the reduced salt. Interestingly, the voltammetry of the electrochemically placed deposits of TCNQ [11, 14] also reveals the presence of diffusion at fast scan rates (short redox cycling times), implying that these deposits also are not in the energetically favourable state required for the nucleation-growth process (developed after the redistribution reaction) to occur.

When TCNQ is mechanically adhered to a highly polished glassy carbon electrode, in situ AFM experiments reveal that a random array of sizes and spacing of TCNQ particles are present on the electrode surface

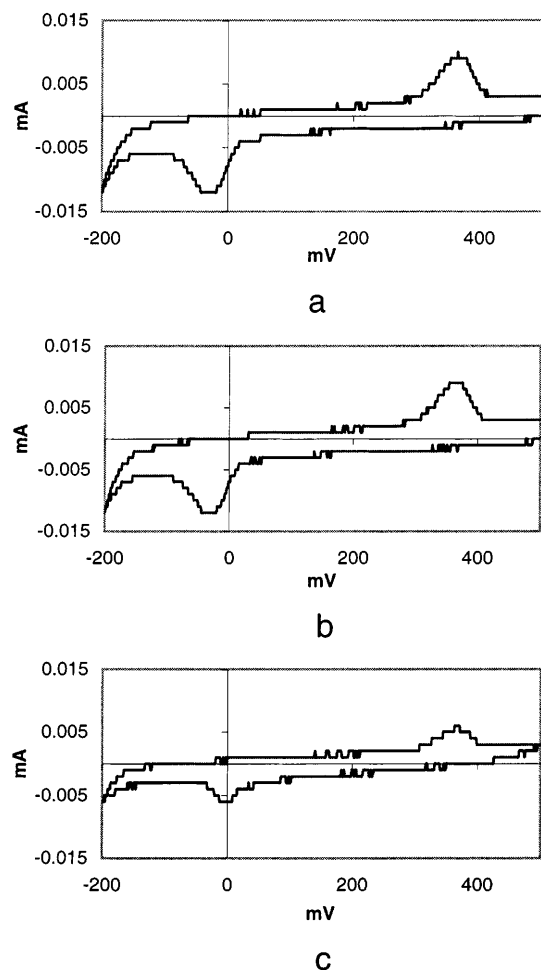
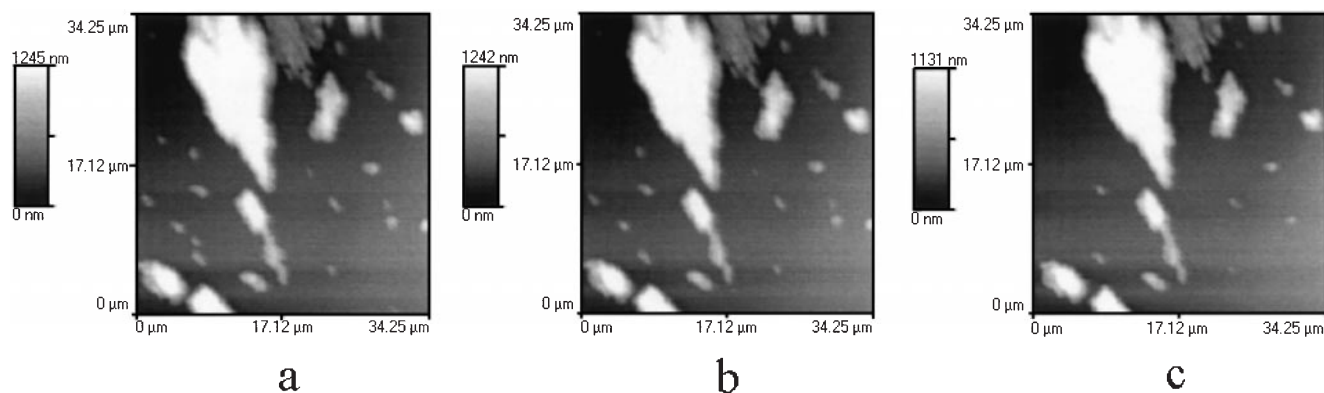


Fig. 6 Voltammograms obtained after almost amorphous TCNQ is mechanically attached to a glassy carbon electrode which is then placed in 0.1 M Et_4NCl (**a** first, **b** third and **c** tenth scan, respectively). The scan rate was 0.1 V s^{-1} and the reference electrode was Ag/AgCl (0.1 M electrolyte)

Fig. 7 In situ AFM images of the $[\text{TCNQ}]^{0/-}$ system attached to a glassy carbon electrode obtained at 0.4 V when 0.1 M Et_4NCl is the electrolyte after **a** 0, **b** 1 and **c** 2 potential cycles at a scan rate of 0.1 V s^{-1} between 0.5 V and -0.2 V . The reference electrode was Ag/AgCl (0.1 M electrolyte)



(Fig. 2). An analogous result has been reported via ex situ electron scanning microscopy experiments at a gold electrode [15, 16]. When the electrode containing adhered TCNQ solid is placed in contact with an aqueous (electrolyte) medium, a wide range of energy states can be assigned to the mechanically attached particles [15, 16] and probably electrochemically formed particles [11, 14]. On application of a sufficiently negative potential in the initial reductive part of the redox cycle, some of the reduced TCNQ salt generated at the electrode-solid-aqueous (electrolyte) interface may diffuse into the interfacial region, where the concentration of solution soluble material is thermodynamically limited by the solubility product. At the interface, the dissolved form of the reduced salt can either irreversibly diffuse into the diffusion layer or, after saturation or supersaturation has been achieved, reprecipitate onto the electrode surface in an energetically more favourable form. Since TCNQ salts are only slightly soluble [8, 20], saturated solutions can be readily formed in the interfacial region during the course of redox cycling experiment.

The “tailing” in the current observed after the peak value has been reached in the initial reduction component of the cyclic voltammograms and the finite current present in the “inert region” are all consistent with the initial redox-induced formation of a solution soluble TCNQ^- phase detected with 0.1 M KCl or CsCl electrolyte. Experiments at a rotated ring disk electrode and in situ ESR-spectroelectrochemical experiments when a KCl electrolyte is used also are consistent with formation of a low concentration of TCNQ^- in the interfacial region [17]. Cycling of the potential can then lead to a dissolution-precipitation sequence in the interfacial region, which enables the redistribution reaction to occur on the electrode surface. This newly formed crystalline material, which is still attached to the electrode surface, is presumably in an energetically lower state than the initially almost amorphous form of the solid material. This suggested mechanism for the redistribution reaction implies that it is the crystalline material which gives the nucleation growth process detected by the voltammetric experiments when redox cycling take place at a scan rate of 0.1 V s^{-1} .

In summary, a redistribution reaction, involving recrystallization of initially almost amorphous TCNQ,

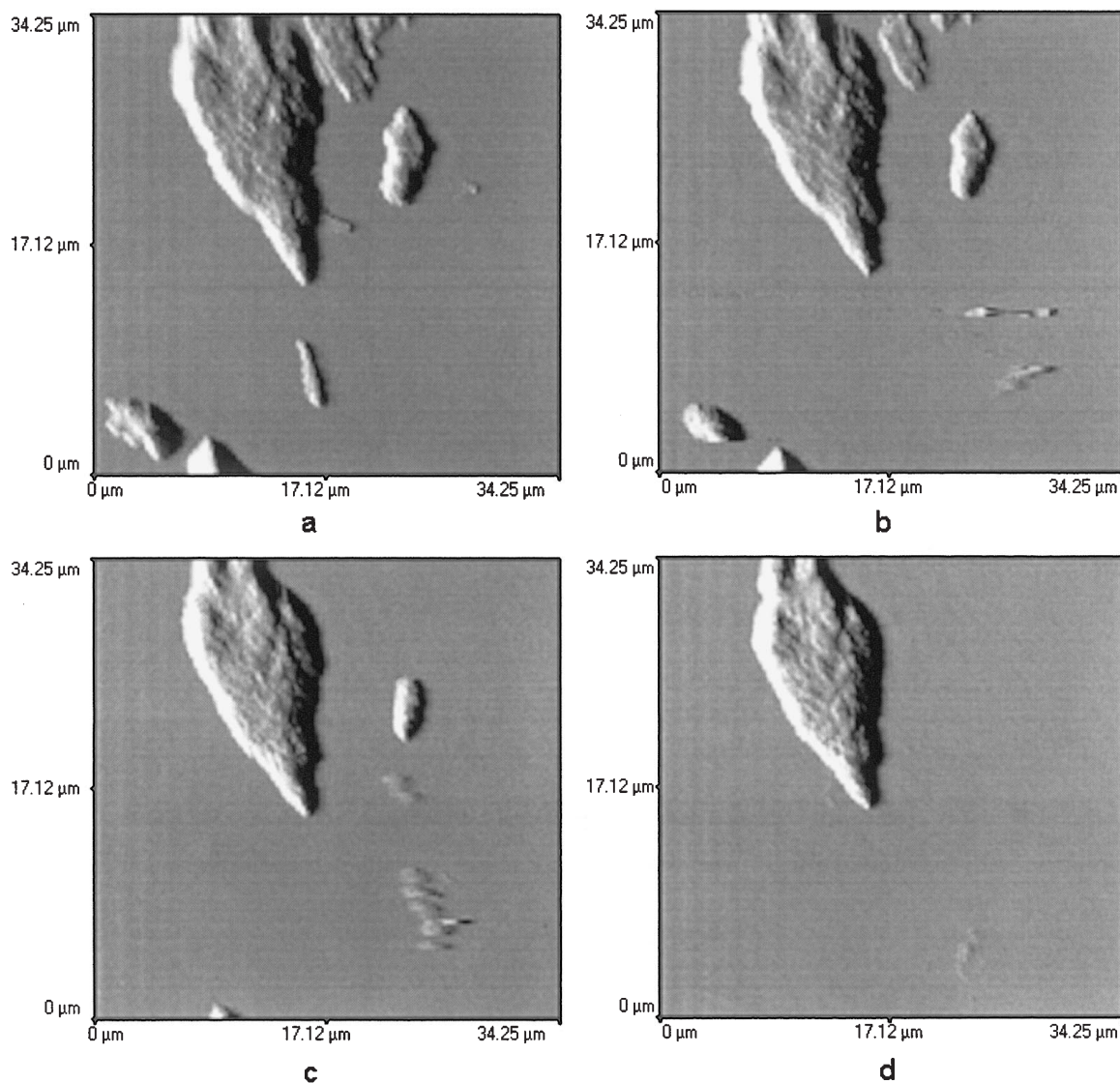


Fig. 8 Sequence of shaded in situ AFM images obtained after **a** 0 s, **b** 162 s, **c** 324 s and **d** 486 s when initially almost amorphous TCNQ is attached to a glassy carbon electrode and the potential is stepped from 0.5 V to -0.2 V when 0.1 M Et_4NCl is the electrolyte. The roughness of the shaded AFM images is approximately $2 \mu\text{m}$. The reference electrode was Ag/AgCl (0.1 M electrolyte)

enables significant features of the voltammetry of $[\text{TCNQ}]^{0/-}$ couple process to be rationalized as follows.

1. The non-reproducibility found with the first few cycles of the potential is associated with a redistribution of solid material, probably by partial dissolution and reprecipitation of reduced TCNQ^- . This redistribution process enables the transformation to occur from a relatively high energy surface state of immobilized and almost amorphous solid to a lower energy surface state of attached microcrystals. The latter form of attached microcrystals undergo significantly less dissolution during the course of redox cycling at a scan rate of 0.1 V s^{-1} and provide the
2. ideal voltammetric response associated with the nucleation-growth solid-state transformation shown in Fig. 1.
2. After conversion to the more microcrystalline state, voltammograms are stable in the sense that peak positions and wave shape become independent of the number of redox cycles. However, a decrease in the current magnitude of the response may still arise from loss of material out of the diffusion layer.
3. The relative rates of the physical processes of solubility, crystallization and diffusion, the strength of adhesion of solid to the electrode surface and the voltammetric scan rate [11] appear to be important factors contributing to the nature of the observed voltammetric response at early stages of redox cycling experiments.
4. The suggestion of a dissolution process at the early stages of redox cycling is consistent with the presence of both solution and solid state phase TCNQ^- detected in the interfacial region during rotating disk

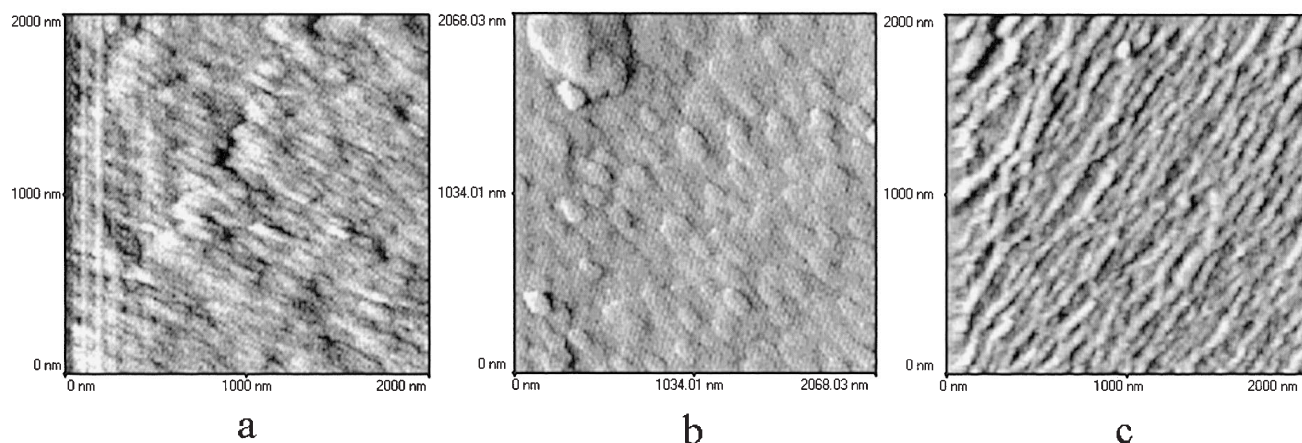
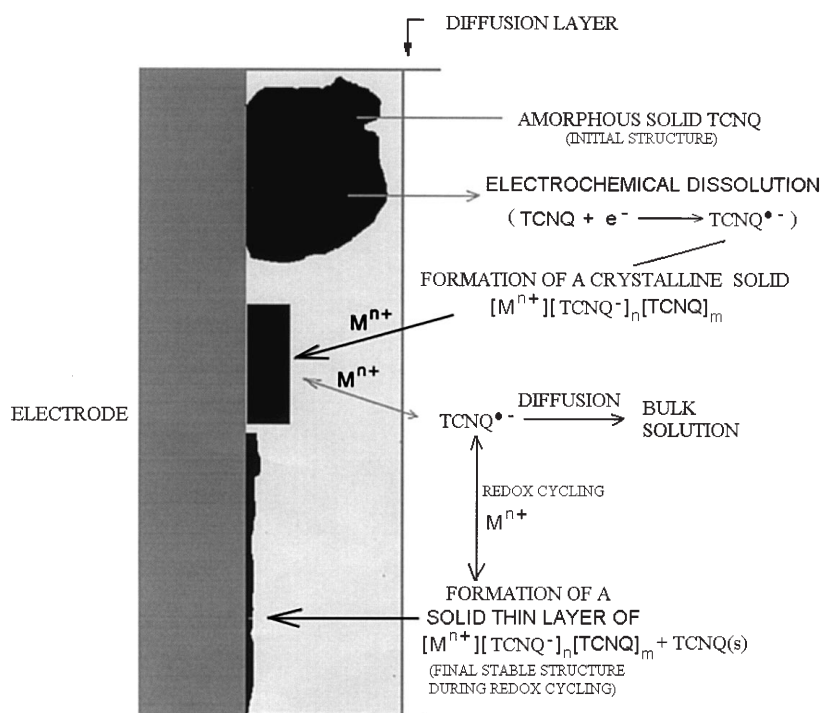


Fig. 9 In situ AFM images at 0.4 V versus Ag/AgCl of the thin layer of TCNQ formed after redox cycling of initially almost amorphous TCNQ mechanically attached to a glassy carbon electrode: **a** polished glassy carbon electrode, **b** surface with 0.1 M KCl as the electrolyte and after 5 potential cycles between 0.4 V and -0.2 V and **c** with 0.1 M CsCl as the electrolyte and after 20 potential cycles between 0.4 V and 0.2 V. The roughness of the shaded images are **a** 12 nm, **b** 20 nm and **c** 46 nm. The scan rate was 0.1 V s^{-1} and the reference electrode was Ag/AgCl (0.1 M electrolyte)

electrode and in situ electrochemical-ESR spectro-electrochemical experiments [17].

- After a period of redox cycling, the response shown in Fig. 1 can be achieved. This response can be explained adequately by a simple nucleation-growth mechanism, where the reduced and oxidized phases can be interconverted without the need to involve the presence of a dissolution process.

Fig. 10 Schematic form of representation of the mechanism proposed to account for the electrochemical conversion of almost amorphous particles of solid TCNQ to surface-attached microcrystals during the initial stages of redox cycling experiments at a glassy carbon electrode



- The time (cycle number) dependence of the voltammetric response on the electrolyte composition also is explained by the presence of an initial redistribution process and the subsequent formation of a stable solid crystalline phase on the electrode surface, which is more structurally suited to electrochemical inter-conversion between the oxidized and reduced forms of the solid.
- Many of the features observed under fast scan rate cyclic voltammetry (0.1 V s^{-1}) appear to be present irrespective of whether the solid is generated by electrochemical oxidation of [9-aminoacridinium (TCNQ) $_2$] [11, 13] or by direct adherence of solid TCNQ [15–17]. This suggests that the redox cycling generates the required energetic state for the nucleation-growth mechanism predominant in long-time domain experiments.

Conclusions

The in situ AFM technique has been shown to be an ideal technique for the study of surface reactions involving morphology changes that occur rapidly during the course of voltammetric redox cycling experiments on solids adhered to an electrode surface. In the present study, features of the mechanism associated with the electrochemical conversion from almost amorphous solid TCNQ to surface-attached microcrystals that occur at the early stages of redox cycling have been identified by in situ AFM measurements and have enabled the model contained in Fig. 10 to be proposed to explain the unstable voltammetric response observed at the early stages of the experiments. The well-defined voltammetric response obtained after conversion to surface-attached microcrystals is explicable in terms of a nucleation-growth mechanism proposed previously on the basis of ex situ electron scanning and X-ray diffraction studies [15, 16].

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