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Mass transfer effects on the electropolymerization current efficiency of 3-methylthiophene in the magnetic field

**Nicholas Leventis · Amala Dass ·
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Abstract 3-Methylthiophene was chosen as a representative conducting polymer precursor, whose electropolymerization proceeds through the coupling of cation radicals. The density of the solution that contains electrogenerated 3-methylthienyl radicals and early oligomers is higher than the density of the surrounding solution, and at low (<0.2 M) monomer concentrations the diffusion layer falls, compromising the electropolymerization current efficiency. Applying a homogeneous magnetic field (3.0 T) perpendicular to the electrode surface ($\theta=0°$) produces concentration gradient paramagnetic forces ($F_{\nabla C}$) that hold the diffusion layer in contact with the electrode. This gives time for more oligomers to get oxidized and for more cation radicals to couple so that the current efficiency increases from 0.028 to 0.037 at 0.05 M of monomer concentration, and from 0.051 to 0.071 at 0.1 M. With the magnetic field parallel to the electrode surface ($\theta=90°$) Lorenz forces causing magnetohydrodynamic convection, in combination with $F_{\nabla C}$ forces keeping the flow pattern in contact with the electrode, increase the current efficiency even more, to 0.048 at 0.05 M of monomer concentration, and to 0.076 at 0.1 M. At higher monomer concentrations (>0.2 M), the rate of radical coupling is evidently fast enough so that, even in the absence of a magnetic field, no natural convection effects are observed and the current efficiency (0.7–0.8) is not affected by the magnetic field.

Keywords Electrodeposition · Magnetic field ·
3-Methylthiophene · Paramagnetic · Forces

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Introduction

The magnetic field has been studied as a variable of the polymerization process, the goal being to control the optical, mechanical, electric, and magnetic properties of the resulting materials [1, 2]. In this regard, there are two main effects that may play a role. The first is traced to the magnetic alignment induced by the anisotropic magnetic susceptibility of reactants. That is, favorable alignment may influence the product morphology or even decrease the activation barrier and accelerate the process. The second effect that may affect reaction kinetics and distribution of products recognizes that in the solvent cage only singlet radical pairs can combine or disproportionate; thereby, it depends on the influence of the magnetic field on coordinated spin motion that in turn controls singlet–triplet transitions (intersystem crossing) of radical pairs [3, 4]. The dual magnetic field effect on the dynamics of both radical spin and molecular relaxation are best exemplified by several radical-initiated graft polymerization processes, like, for example, that of acrylamide into lignocellulose, whereas increases in both the rate and the conversion efficiency have been reported [5, 6]. In other instances (e.g., grafting of methylmethacrylate onto polyvinylalcohol under UV/benzophenone initiation) a marked increase in the graft ratio and the stereoregularity (up to 85%) was observed [7]. Overall, characteristics that have been affected by the magnetic field include the molecular size of the polymer (magnetic field favors termination by combination over disproportionation) and the molecular ordering with concomitant effects upon the point of thermal decomposition, glass transition temperature, viscosity, and mechanical properties [1].

In the electrochemical preparation of conducting polymers, chain growth is usually induced by electrochemical oxidation of the monomers. The most frequently reported

magnetic effect is molecular ordering when a magnetic field is applied parallel to the electrode surface, while the opposite effect has been reported when the field is applied in the orthogonal direction. For example, using wide-angle X-ray diffraction, Osawa et al. reported orientation of polythiophene chains parallel to the direction of the electrode surface at higher electroplating current densities than the upper limit in the absence of the magnetic field; in contrast, a perpendicular arrangement of the electrode surface and the magnetic field inhibited molecular ordering [8]. Similarly, working with polyaniline, Wan and Yang reported differences in the film morphology [9], while, using X-ray diffraction, Cai et al. have shown decreased d-spacing, small degree of orientation in the amorphous regions, and more compact films synthesized in magnetic fields parallel to the electrode surface; in the same systems, the orientation brought about by the magnetic field seems to have decreased the energy barrier for charge transport, and polyaniline films grown in a magnetic field were reportedly more conducting [10]. In the same vain, using atomic force microscopy, Inoue et al. observed smoother poly(o-phenylynediamine) (PoPD) films when the field was applied parallel to, and rougher when the field was applied perpendicular to, the electrode surface; the smoothness of films grown in the absence of field was between the two extremes [11]. The film smoothness at the parallel orientation was attributed to magnetohydrodynamic (MHD) stirring, while the roughness was associated with the diamagnetic properties of PoPD. Both the MHD effect and diamagnetic orientation have been also evoked by Mogi and Kamiko in conjunction with the diffusion-limited aggregation model to explain the magnetic effect on the electrodeposition of polypyrrole in thin cells, and the change of the appearance of the deposit from a fractal morphology into a compact film [12, 13]. More intriguing, however, have been magnetic field-induced changes in the peak-current potential of polypyrrole films doped with p-toluenesulfonate anions. Those changes have been attributed to both the diamagnetic orientation of molecular chains and the magnetically induced slow change in the alignment of the polymer chains during repetitive redox cycling (doping and undoping) [14–16].

Meanwhile, diamagnetic orientation notwithstanding, it is well-understood that oxidative electrochemical polymerization proceeds through cation-radical intermediates [17]. Thus, apart from the fact that the prerequisite for magnetic sensitivity of chemical reactions is the presence of radicals [18], radicals, being paramagnetic species, experience paramagnetic forces, which may be translated into body forces upon the volume of the solution that contains them [19, 20]. However, body forces on the electrolytic solution are associated with convective phenomena. Consequently, despite the possible role of molecular paramagnetism on polymer orientation and ordering, paramagnetic body forces may assist, prevent, or modify other convection mechanisms like, for example, MHD stirring or natural convection [21–28]. To our knowledge, the role of the paramagnetic body forces on mass transport during electropolymerization has not been investigated. In this study we use the current efficiency as a metric of how much radical is generated during electrodeposition vs how much ends up in the polymer film, and we look at the role of the paramagnetic body forces on the electrodeposition of conducting polymers, using poly(3-methylthiophene) as a representative example.

Materials and methods

Anhydrous CH_3CN and 3-methylthiohene were purchased from Aldrich and were used as received. Tetrabutylammonium perchlorate (TBAP) was synthesized and dried as described before [29]. Bent Pt working electrodes (Scheme 1) were made by sealing with epoxy 1.0 mm diameter Pt wires (Alfa-Aesar, Ward Hill, MA, USA) at the tip of bent glass tubes according to procedures described recently [28]. Under the convention of Scheme 1, $\theta=0°$ when the electrode surface is perpendicular to the magnetic field, and $\theta=90°$ when the electrode surface is parallel to the magnetic field. A Pt mesh was used as a counter electrode, while an aqueous Ag/AgCl electrode (CH Instruments, Austin, TX, USA) was used as reference. All electrochemical experiments were conducted with a Perkin-Elmer 263A potentiostat controlled by the Perkin-Elmer (Wellesley, MA, USA) model 270/250 Research Electrochemical Software 4.30. The magnetic field was generated by an electromagnet constructed around two iron poles 9 cm in diameter, extending 4.5 cm out of the copper coils, leaving a 3-cm gap between them. The two poles were mounted with iron posts on a 2-in.-thick iron base plate. The copper coils were powered with a Kepco (Flushing, NY, USA) power supply, model JQE 150-1.5, with a maximum DC output of 1.5 A. The intensity of the magnetic field was measured with a Gaussmeter model GM1A manufactured by Applied Magnetics (Baltimore, MD, USA). With the power supply at the maximum DC output, the field generated in the gap between the centers of the two poles

Scheme 1 A bent Pt disk electrode and the orientation angle θ relative to the direction of the magnetic field **B**
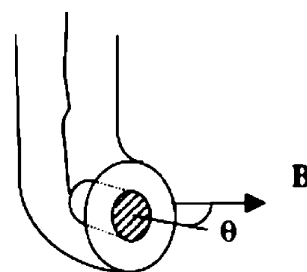
was 3.3 T. That field was 3.24 T 1 in away from the center of the poles (a 1.8% decrease). Thus, the magnetic field across the 1.00-mm diameter of the disk electrodes placed near the center of the gap and facing the magnetic field (θ=0°) is, for all practical purposes, homogeneous within 0.23%.

All electrochemical experiments were carried out with 5–10 mL of the appropriate electrolytic solutions in Wheaton scintillation vials (Fisher, Hampton, NH, USA) under Ar. The monomer concentration was varied and polymer was deposited potentiostatically (1.85 V vs Ag/AgCl) in the absence of a magnetic field and at different orientations of the bent electrode relative to the magnetic field (at θ=0°, 90°, 180°, and 270°). The cyclic voltammetric characterization of the poly(3-methylthiophene) films was conducted in the absence of a magnetic field.

Results

Poly-3-methylthiophene was deposited for 30 s on bent Pt disk electrodes (1 mm in diameter, Scheme 1) by potential step chronoamperometry at 1.85 V vs aq Ag/AgCl in CH$_3$CN solutions containing 0.1 M TBAP as supporting electrolyte and variable monomer concentrations. The deposition potential was chosen 200 mV more positive than the peak current of the monomer voltammogram at 0.1 V s^{-1}, but still below the range of irreversible overoxidation (>2.0 V vs Ag/AgCl). A homogeneous magnetic field of 3.0 T was applied with its vector normal (θ=0° and 180°) or parallel (θ=90° and 270°) to the electrode surface. Figure 1 shows typical deposition current–time curves at three different concentrations and at two different orientations of the magnetic field (θ=0° and 90°). At θ=180° and 270°, the results were identical to those at 0° and 90°, respectively, and are not shown. With the concentration of 3-methylthiophene at 0.05 or 0.1 M (Fig. 1a,b), all orientations of the magnetic field seem to accelerate the oxidation of the monomer (higher currents relative to the deposition curves in the absence of the field). On the other hand, at the higher monomer concentration (0.2 M), the magnetic field had practically no effect (Fig. 1c).

Looking at the Pt disk electrode during electrodeposition in a 0.05-M monomer solution in the absence of the magnetic field (Fig. 2a), we see that the purple diffusion layer that contains early oxidation products of 3-methylthiophene separates from the electrode and falls, implying that its density is higher than the density of the surrounding solution. In turn, Fig. 2b shows that when a magnetic field is applied normal to the electrode surface (at θ=0°), density-driven natural convection is halted and the colored layer remains in contact with the electrode. Similar observations are made at
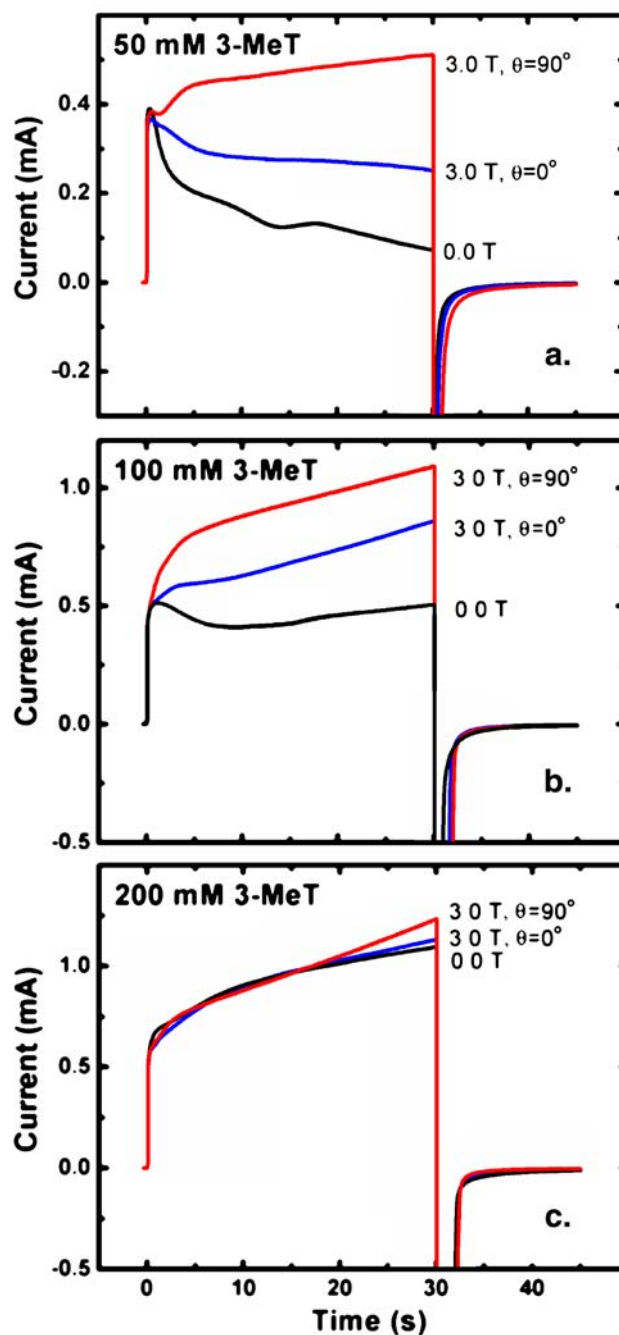
Fig. 1 Current–time curves for the deposition of poly(3-methylthio-phene) on 1.0-mm-diameter Pt bent electrodes (see Scheme 1) from argon-degassed CH$_3$CN/0.1 M TBAP solutions containing the monomer concentrations shown in the frames. The lines are color-coded for the presence of a magnetic field and its orientation relative to the electrode (Scheme 1)

other orientations of the electrode relative to the field. Eventually, when the monomer concentration is $\geq$ 0.2 M, we observe no natural convection like that shown in Fig. 2a, even in the absence of the magnetic field.

Figure 3 presents the characterization voltammograms of poly-3-methylthiophene films deposited at various
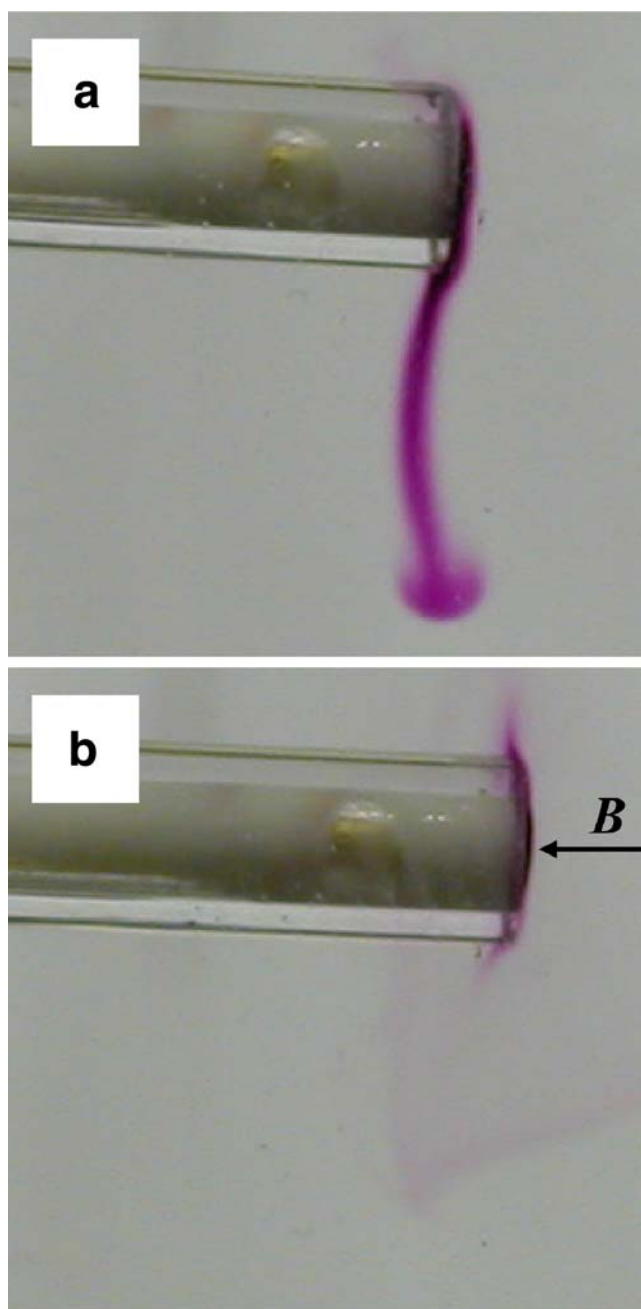
Fig. 2 Photographs 15 s after a potential step at 1.85 V vs Ag/AgCl of a Pt disk electrode (side view) in a CH₃CN/0.1 M TBAP solution containing 50 mM of 3-methylthiophene. **a** In the absence of a magnetic field. **b** In the presence of a 3.0-T field perpendicular to the electrode surface ($\theta=0°$, refer to Scheme 1)

monomer concentrations in the absence and in the presence of a magnetic field at various orientations. All voltammetry was conducted at 0.1 V s^{-1} in fresh electrolyte (CH₃CN/0.1 M TBAP) in the absence of a magnetic field. Of course, it is apparent immediately that with 0.05 and 0.1 M of monomer concentration during electrodeposition in the magnetic field (any orientation),

the coverage is higher than what is achieved by electrodeposition in the absence of the magnetic field. Furthermore, it is hardly surprising that the coverage (as estimated by the area under the voltammograms in Fig. 3) follows the same trend as the magnitude of the corresponding deposition current in Fig. 1. From that perspective, with monomer concentrations higher than about 0.2 M, electrodeposition in the presence or absence of a magnetic field makes no difference in the amount of polymer accumulated on the electrode, which is in agreement with the corresponding current–time deposition characteristics of Fig. 1.

However, what is not immediately obvious from Figs. 1 and 3 is the current utilization efficiency. The latter is calculated by dividing the charge used for the oxidation of the polymer (i.e., half of the charge under the cyclic voltammograms of Fig. 3) by the charge consumed for the electrodeposition process (that is, the integral under the current–time curves of Fig. 1). The results are summarized in Table 1. The current efficiency is related to whether the charge consumed for oxidation of the monomer results in more or less polymer formed in the presence or absence of the magnetic field. In turn, that would be an indication of whether the magnetic field prevents or facilitates the dispersion of radicals, thus accelerating or inhibiting coupling to form the polymer.
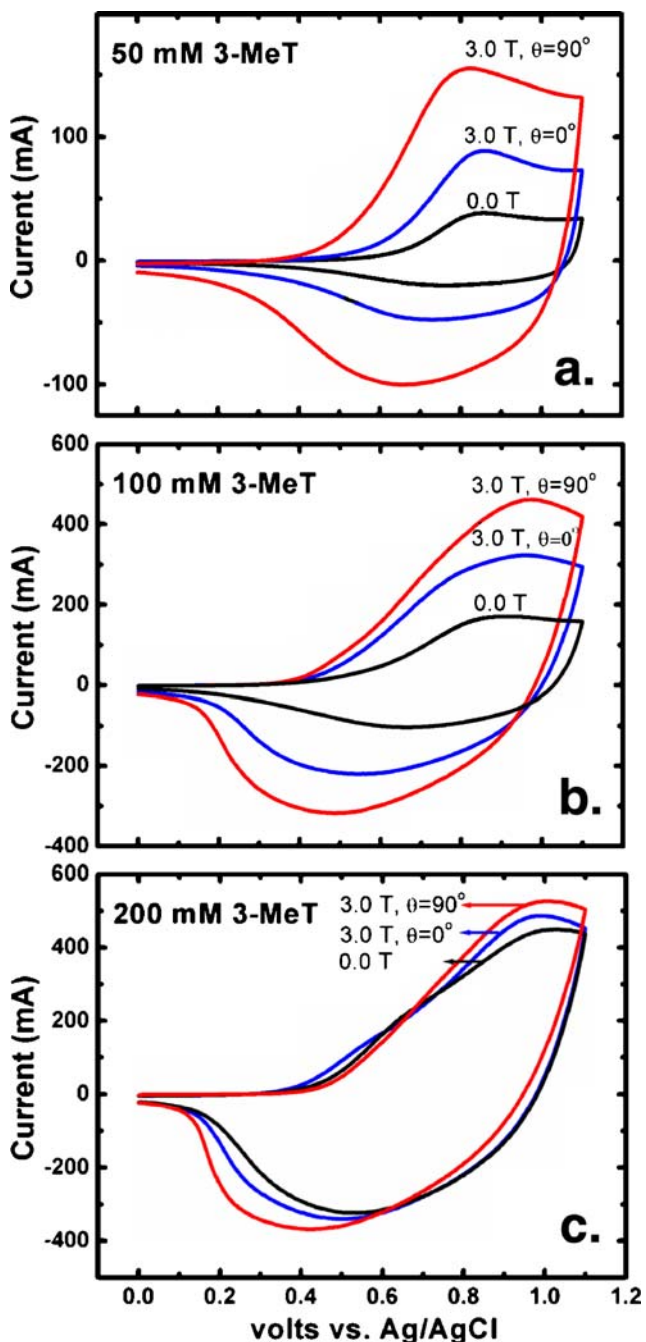
Clearly, at 0.05 and 0.1 M of monomer concentration in the electrodeposition solution, the magnetic field improves the current efficiency, and it does so more effectively when the electrode surface is oriented parallel ($\theta=90°$), rather than perpendicular ($\theta=0°$), to the field. The latter was rather unexpected (see "Discussion" section below), and to deconvolute the MHD from the paramagnetic effect, we conducted control experiments using a 0.05-M solution of 3-methylthiophene and a rotating electrode (0.229 cm in diameter) as a model of a purely convective system. The potential of the electrode was stepped from zero to +1.85 V vs Ag/AgCl, and it became evident that by forced convection alone, the current efficiency always decreased (from 0.039 at 0 rpm to 0.033 at 10 rpm, to 0.017 at 20 rpm to 0.016 at 50 rpm and above), despite the fact that the oxidation current was higher for faster rotation rates.

Discussion

Review of the body forces in electrolytic solutions

According to classical electromagnetic theory, all possible magnetic forces in the electrolytic continuum should be traced to forces on moving charges and magnetic dipoles.

Fig. 3 Characterization voltammograms at 0.1 V s^{-1} in CH$_3$CN/ 0.1 M TBAP solutions in the absence of a magnetic field of poly(3-methylthiophene) films deposited on 1.00-mm-diameter Pt bent electrodes under the conditions shown in the frames

Table 1 Current efficiency from potential step electrodeposition (30 s, 1.85 V vs Ag/AgCl) of poly(3-methylthiophene) at various monomer concentrations on a disk electrode (1 mm diameter) at different orientations relative to an applied magnetic field

	Monomer concentration				
	0.05M	0.1M	0.2M	0.5M	1.0M
	Current efficiency				
$\|\boldsymbol{B}\|=0$	0.028	0.051	0.071	0.078	0.073
$\|\boldsymbol{B}\|=3T;\ \theta=0°$	0.037	0.071	0.077	0.079	0.071
$\|\boldsymbol{B}\|=3T;\ \theta=90°$	0.048	0.076	0.072	0.076	0.069

In an electrochemical cell, cations and anions move in opposite directions. However, even though their velocities, $\boldsymbol{v}_+$ and $\boldsymbol{v}_-$, point in opposite directions, the corresponding charges have opposite signs; therefore, the products $Q_+\boldsymbol{v}_+$ and $Q_-\boldsymbol{v}_-$ have the same sign, and cations and anions experience magnetic forces *in the same direction*. The consequence of this asymmetry is that, through collisions with the solvent molecules, cations and anions transfer momentum to the surrounding solvent, resulting in a magnetic force manifested macroscopically on the segment of the electrolytic conductor that carries ionic current. Formally, the total Lorenz force acting on a unit volume element of the electrolytic conductor is the sum of the force acting upon all moving ions in that volume and is given by Eq. 2, where

$$\boldsymbol{F}_B = (n_+ Q_+ \boldsymbol{v}_+ + n_- Q_- \boldsymbol{v}_-) \times \boldsymbol{B} \qquad (2)$$

n_+ and n_- are the concentrations in units of particles per unit volume of the cations and anions, respectively. But, $(n_+ Q_+ \boldsymbol{v}_+ + n_- Q_- \boldsymbol{v}_-)$ is the current density $\boldsymbol{i}$ flowing through the electrolytic conductor, so we arrive at the familiar macroscopic expression for the MHD force on the unit volume element of the electrolytic conductor:

$$\boldsymbol{F}_B = \boldsymbol{i} \times \boldsymbol{B} \qquad (3)$$

Forces due to magnetic dipoles

The average low-field magnetic moment per magnetic dipole of species "j" with spin 1/2 (that includes all common organic radicals) is given by

$$< \boldsymbol{m} >_j = \left(\frac{g\mu_B}{2}\right)^2 \frac{\boldsymbol{B}}{kT} \qquad (4)$$

where k is the Boltzmann constant, T the absolute temperature, g the Lande g factor, and μ_B the Bohr magneton. In turn, the average magnetic energy per dipole "j," $<U_{M>j}$ is given by Eq. 5.

$$< U_M >_j = - < \boldsymbol{m} >_j \cdot \boldsymbol{B} \qquad (5)$$

Forces due to moving charges

The Lorenz force on a moving charge, Q, in a magnetic field is proportional to the charge and the cross product of its velocity, $\boldsymbol{v}$, and the magnetic flux density $\boldsymbol{B}$ (Eq. 1).

$$\boldsymbol{F}_L = Q\boldsymbol{v} \times \boldsymbol{B} \qquad (1)$$

Because the unit volume element of the electrolytic solution contains $C_j N_A$ dipoles of species "j," where C_j is the concentration of species "j" and N_A is Avogadro's number, the total magnetic energy is given by

$$U_{M,j}\Big|_{per\ unit\ volume} = -N_A C_j < \boldsymbol{m} >_j \cdot \boldsymbol{B} \qquad (6)$$

The force acting on the unit volume element because of its paramagnetic properties, $\boldsymbol{F}_{pm}$, is derived through $\boldsymbol{F}_{pm} = -\boldsymbol{\nabla} U_{M,j}\big|_{per\ unit\ volume}$, and because there are two quantities that may vary in space, $\boldsymbol{B}$ and C_j, the total paramagnetic force is given as a sum:[1]

$$\boldsymbol{F}_{pm} = 2N_A C_j \left(\frac{gm_B}{4}\right)^2 \frac{\boldsymbol{B} \cdot \boldsymbol{\nabla B}}{kT}$$
$$+ N_A \left(\frac{gm_B}{4}\right)^2 \frac{|\boldsymbol{B}|^2}{kT} \boldsymbol{\nabla} C_j \qquad (7)$$

The first term in Eq. (7) describes the field gradient paramagnetic force, $\boldsymbol{F}_{\nabla B}$, which is exerted in the presence of paramagnetic species in areas where the magnetic field gradient $\boldsymbol{B} \cdot \boldsymbol{\nabla B} \neq 0$. Such field gradients may arise from nonhomogeneous applied fields or in the vicinity of ferromagnetic objects in homogeneous fields. The latter case is more prominent because the field gradients around small magnetizable ferromagnetic objects (e.g., ferromagnetic microwire electrodes) can be very high.[2]

The second term in Eq. (7) describes the concentration gradient paramagnetic force, $\boldsymbol{F}_{\nabla C}$, which can be present even in homogeneous fields and is exerted upon volumes of the electrolytic solution that contain a concentration gradient of radicals. When the redox-active species is a diamagnetic organic molecule, such as 3-methylthiophene, a concentration gradient of radicals is generated in the diffusion layer, and, as a result, it experiences $\boldsymbol{F}_{\nabla C}$ forces. It is noted also that although their effect may be masked by other phenomena, as, for example, by MHD convection, $\boldsymbol{F}_{\nabla C}$-type forces are always present wherever there is a diffusion layer of paramagnetic species, and their magnitude (per unit volume) is typically much larger than that of $\boldsymbol{F}_B$.[3]

In the experimental design of this study, we chose to work in a homogeneous magnetic field with nonferromagnetic electrodes (Pt). Thus, depending on the orientation of the electrode relative to the magnetic field, we may have to deal with $\boldsymbol{F}_{\nabla C}$ forces only (at $\theta = 0°$ and $180°$) or with the coexistence of $\boldsymbol{F}_B$ and $\boldsymbol{F}_{\nabla C}$ (at $\theta = 90°$ and $270°$). In no case do we expect involvement of $\boldsymbol{F}_{\nabla B}$-type of paramagnetic forces.

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[1] Because $\boldsymbol{F}_{pm}$ is derived as the gradient of energy, it has been also represented as $\boldsymbol{F}_\nabla$ [19, 25, 27].

[2] For a brief discussion of the issue, with estimates of field gradients around small ferromagnets, see Leventis and Gao [25], p 1082.

[3] For a relative magnitude analysis of $\boldsymbol{F}_B$ and $\boldsymbol{F}_{\nabla C}$, see footnote 24, p 3987, in Leventis and Gao [19].

Mass transfer effects during electropolymerization of 3-methylthiophene in the magnetic field

Albeit not quantitatively, acceleration of the polymer accumulation by electropolymerization in the magnetic field has been reported before. Specifically, Wan and Yang have observed a linear relationship between $\log I_{max}$ and $\log N$ during electrodeposition of polyaniline (where I_{max} is the maximum voltammetric current during a potential sweep and N is the count-number of the potential sweep), and they reported that the slope of that liner relationship increased when electrodeposition was carried out in the magnetic field [9]. However, from a practical perspective, an equally important question is whether the electropolymerization current is used more efficiently or less so in the presence of a magnetic field.

It is well established that electrodeposition of poly(3-methylthiophene) proceeds through the one-electron oxidation of the monomer, followed by coupling of cation radicals (Scheme 2) [17, 30]. According to Fig. 2a, the density of the electrolytic solution in the vicinity of the electrode that contains the purple 3-methylthienyl cation radicals is higher than the density of the surrounding bulk electrolyte, and it falls. That generates stirring that accelerates the mass transfer of the redox-active substance (the monomer in this case) to the electrode. At the same time, however, the electropolymerization current efficiency is expected to be compromised because of the convective removal from the vicinity of the electrode of a large portion of the electrogenerated cation radicals. As far as the shape of the current–time curves is concerned, it has been established that stirring generated by falling "diffusion" layers causes deviations from the ideal diffusion-control (Cottrell) behavior, and the current–time curve declines to a steady state [25, 27]. This is approximately the case for 0.05-M solutions in the absence of a magnetic field (Fig. 1a—black line). In general, however, the current increases with time (Fig. 1b,c—black lines), mainly because the cation-radical coupling product looses two protons and the resulting neutral oligomer is redox-active and is oxidized anew (Scheme 2). Thus, the current is supported not only by fresh 3-methylthiophene transported from the bulk to the electrode, but also by the very product of the coupling process, which is also electroactive on its own right. Overall, an increase in the deposition current signifies that more oligomer is captured and oxidized further to conducting polymer than what escapes in the bulk due to natural convection.

Upon application of a magnetic field perpendicular of the electrode ($\theta = 0°$), the cross product $\boldsymbol{i} \times \boldsymbol{B} = 0$, while the dominant force acting upon the diffusion layer is $\boldsymbol{F}_{\nabla C}$ and is directed towards the electrode (that is, the area of higher radical concentration or, equivalently, of higher magnetic

Scheme 2 The mechanism of the oxidative polymerization of 3-methylthiophene [17]
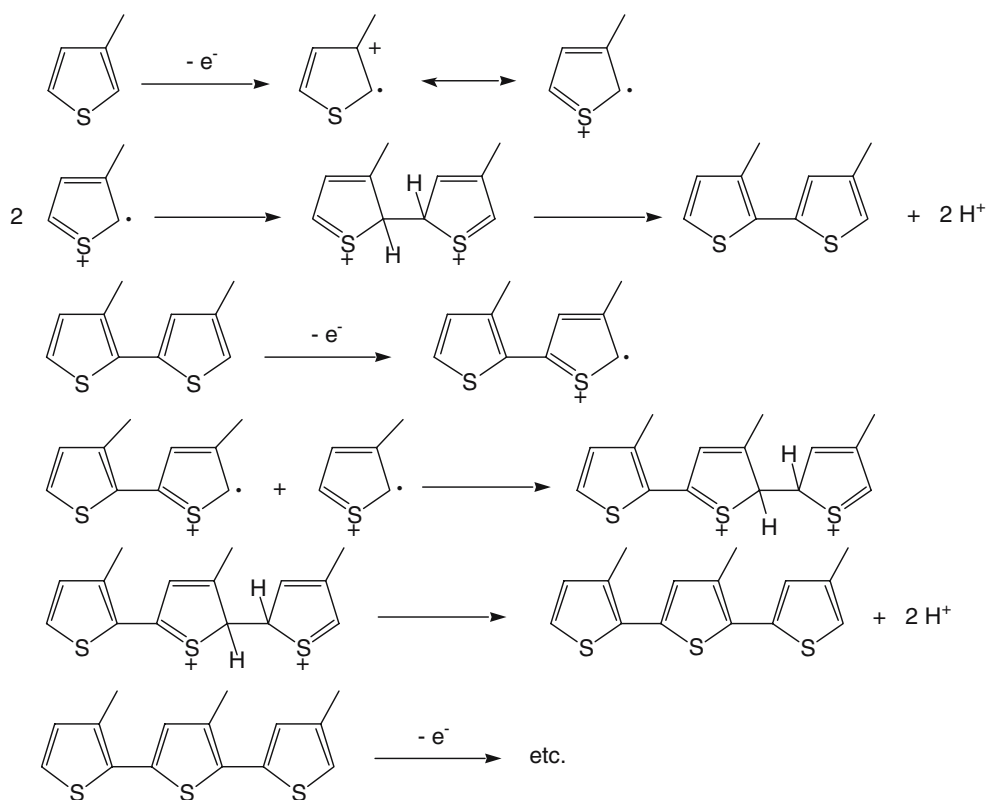
susceptibility). Thus, in agreement with our recent findings [27], $F_{\nabla C}$ holds the diffusion layer (Fig. 2b) against the density-gradient gravitation force, giving time for cation-radicals to meet, react, and form polymer (Scheme 2). An alternative explanation for the increase of the deposition current under B at $\theta=0°$ might involve micro-MHD effects [31], or even confinement due to a possible MHD-rotation around the perimeter of the electrode [32]. As shown by White, however, vortexes due to radial current components at the perimeter of electrodes <0.25 mm in diameter also generate a linear convective fluid flow in the center of the vortex towards the electrode [32]. But, as we have shown recently, 1-mm-diameter electrodes in electrolytic solutions containing 50–100 mM of a redox-active substance show strictly diffusion behavior in magnetic fields with B at $\theta=0°$, thus eliminating all possibilities for convection [27].

So, the cancellation of natural convection with B at $\theta=0°$ is attributed solely to $F_{\nabla C}$.

Now, poly(3-methylthiophene) is redox-active (Fig. 3), with one positive charge developing every four monomer units, assuming ideal 2,5-couplings between monomer units [33]. Scheme 3 illustrates the situation. Evidently, the additional radicals engaged in the polymerization process due to the lack of natural convection when B is at $\theta=0°$ outweigh the loss of additional monomers arriving at the electrode by density-gradient-driven natural convection (when $B=0$), and both the amount of polymer deposited on the electrode with B applied at $\theta=0°$ (blue lines in Fig. 3a,b) and the current efficiency (Table 1) increase. A point that might need some clarification is the fact that even under the best of circumstances the current efficiency is not better than 8%. According to Scheme 2, formation of poly

Scheme 3 Electrochemical oxidation of poly(3-methylthiophene) assuming that one positive charge is developing in every four monomer units [33]
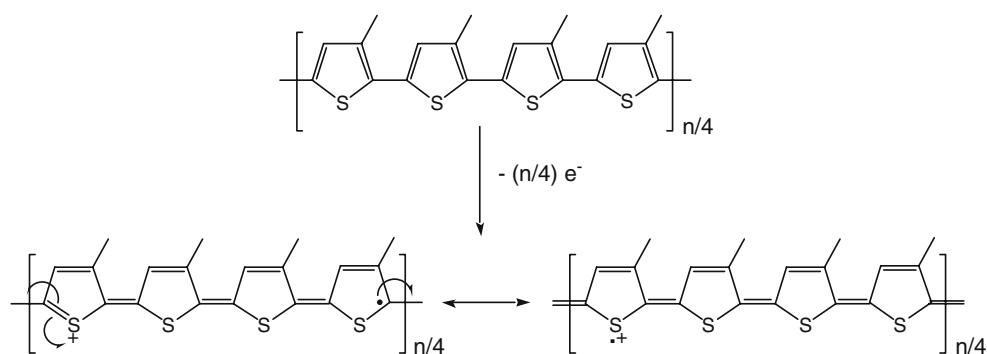
(3-methylthiophene) with "n" monomer units requires $2(n-2)+2$ electrons. According to Scheme 3, the same polymer consumes $n/4$ electrons during its oxidation. Thus, the limit of the current efficiency for $n{\rightarrow}\infty$ is 12.5%. The fact that the experimental current efficiency is even less than 12.5% is probably due to the fact that not all monomer units throughout the polymer couple at the 2,5-positions [17], thereby the polymer stores a little less charge than one electron every four monomer units (actually, 8% current efficiency corresponds to one positive charge per six monomer units).

At $\theta{=}90°$, the cross product $i{\times}B$ is maximized. The resulting MHD force, F_B causes convection, and again as with natural convection, the current–time curve should reach a steady-state [34]. However, it doesn't, and the upward drift of that curve again signifies that more oligomer is oxidized further than what escapes in the bulk. The faster polymer accumulation in this orientation should be related to the faster mass transfer of the monomer to the electrode caused by the MHD mechanism. Under identical experimental conditions, a rotating electrode shows higher oxidation current for faster rates of rotation. But, as presented in the "Results" section, the current efficiency of the 3-methylthiophene polymerization at the rotating electrode decreases as the rotation rate increases, even for very low rotation rates like, for example, 10 or 20 rpm. This decreased efficiency is reconciled based on the fact that rotation "sweeps away" soluble oligomers [35]. Meanwhile, the analogy between a MHD electrode and the rotating electrode as a means of generating convection is rather well understood [34]. Both electrodes accelerate the mass transfer of the monomer towards the electrode, and it has been shown that in a 50-mM solution of a redox active substance in CH_3CN/0.1 M TBAP, a 0.229-cm-diameter electrode generates MHD convection equivalent to ~100 rpm rotation. So, why does the current efficiency of the Pt electrode in the MHD configuration ($\theta{=}90°$) increase? Unlike the rotating electrode, in the MHD electrode there is an additional F_{VC} force acting on the system. As discussed in the "Review of the body forces in electrolytic solutions" section above, F_{VC} still operates within the diffusion layer in front of the electrode, and its direction is normal to the F_B force. The two forces not only are not incompatible, but qualitatively, the role of F_{VC} is to hold the flow pattern generated by F_B in contact with the electrode. Then, the fact that at $\theta{=}90°$ we observe no radical flow past the electrode means that 3-methylthienyl cation radicals within the boundary layer couple faster than the residence time of the volume that contains them over the electrode. Faster transport of monomer to the electrode and capture of all radicals in the form of polymer results in improved current efficiency relative to that obtained at $\theta{=}0°$.

At last, when the monomer concentration is increased above 0.2 M, no natural convection is observed and the effect of the magnetic field on the current efficiency becomes negligible. The absence of magnetic effects, even at $\theta{=}90°$, is consistent with previous observations, whereas when concentration gradients are high (as, for example, during fast-sweep voltammetry), diffusion dominates over MHD effects [34]. Then, consistently with the discussion above, as the radical concentration is increased, the radical combination reaction rate increases and becomes faster than the rate of mass transfer. Overall, under those circumstances, we expect no MHD and no density-driven natural convection effects.

Conclusions

The polymerization efficiency of 3-methylthiophene can be improved by conducting the electropolymerization process in the magnetic field. The highest increase in the efficiency is observed when the electrode surface is parallel to the magnetic field, where we expect MHD mass transport of the monomer to the electrode. This magnetoelectrochemical method of increasing the current efficiency works best with lower monomer concentrations, which may be the situation when the monomer is not readily available.

References

1. Chiriac AP, Simionescu CI (2000) Prog Polym Sci 25:219
2. Landee CP, Melville D, Miller JS (1990) In: Gatteschi D, Kahn O, Miller JS, Palacio F (eds) Magnetic molecular materials, vol 198. Kluwer, Dordrecht, p 395
3. Kaptein R, Oosterhoff JL (1969) Chem Phys Lett 4:195
4. Closs GL (1969) J Am Chem Soc 91:4552
5. Chiriac AP, Simionescu CI, Neamtu I, Popa M (1998) Cell Chem Technol 32:425
6. Chiriac AP, Neamtu I, Cazacu G, Simionescu CI, Rozmarin Gh (1997) Angew Makromol Chem 246:1
7. Junlian H, Wu Q (1990) Chin J Polym Sci 8:108
8. Osawa S, Ogawa T, Ito M (1997) Synth Met 90:109
9. Wan M, Yang J (1995) Synth Met 69:155
10. Cai L-T, Yao S-B, Zhou S-M (1997) J Electroanal Chem 421:45
11. Inoue Y, Yamato M, Kimura T, Ito E (1997) Synth Met 84:435
12. Mogi I, Kamiko M (1996) J Cryst Growth 166:276
13. Mogi I, Kamiko M (1996) Bull Chem Soc Jpn 69:1889
14. Mogi I (1996) Chem Lett 25:419
15. Mogi I (1996) Bull Chem Soc Jpn 69:2661
16. Mogi I, Watanabe K (1997) Bull Chem Soc Jpn 70:2337
17. Roncali J (1992) Chem Rev 92:711
18. Steiner UE, Ulrich T (1989) Chem Rev 89:51
19. Leventis N, Gao X (2001) Anal Chem 73:3981
20. Pullins MD, Grant KM, White HS (2001) J Phys Chem B 105:8989
21. Ragsdale SR, Grant KM, White HS (1998) J Am Chem Soc 120:13461

22. Hinds G, Coey JMD, Lyons MEG (2001) Electrochem Commun 3:215
23. Hinds G, Spada FE, Coey JMD, Ní Mhíocháin TR, Lyons MEG (2001) J Phys Chem B 105:9487
24. Perov NS, Sheverdyaeva PM, Inoue M (2002) J Appl Phys 91:8557
25. Leventis N, Gao X (2002) J Am Chem Soc 124:1079
26. Bund A, Kuehnlein HH (2005) J Phys Chem B 109:19845
27. Leventis N, Dass A (2005) J Am Chem Soc 127:4988
28. Dass A, Counsil JA, Gao X, Leventis N (2005) J Phys Chem B 109:11065
29. Leventis N, Gao X (1999) J Phys Chem B 103:5832
30. Audebert P, Hapiot P (1995) Synth Met 75:95
31. Oshikiri Y, Sato M, Yamada A, Aogaki R (2004) Jpn J Appl Phys 43:3596
32. Grant KM, Hemmert JW, White HS (2002) J Am Chem Soc 124:462
33. Tourillon G (1986) In: Skotheim TA (ed) Handbook of conducting polymers, vol 1. Marcel Dekker, New York, p 293
34. Leventis N, Chen M, Gao X, Canalas M, Zhang P (1998) J Phys Chem B 102:3512
35. Ren X, Pickup PG (2001) Electrochim Acta 46:4177