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Electrochromic films of a methylcarbazole derivative: optimization of polymerization and optical contrast

J. Padilla · T. F. Otero

Abstract The effect of the polymerization potential and time on the electrochemical and optical responses of electrogenerated films of poly-[3,6-bis(2-(3,4-ethylenedioxy) thienyl)-N-methylcarbazole] (PBEDOT-NMCz) was studied. Every electrogenerated film was characterized according to the charge consumed during polymerization, its redox charge density (calculated by integration of a control voltammogram), the efficiency of the polymerization process (defined as the charge consumed during electropolymerization to create one redox site), and its optical contrast. Within the studied polymerization potential range, 0.75 to 2 V, the charge consumed during polymerization increased with the potential, while the efficiency of the polymerization process decreased. The redox site production rate reached a maximum at 1.25 V. The optical contrast of the obtained films remained the same when polymerizing in the range between 0.75 and 1.25 V. Polymerization at more anodic potentials resulted in films of lower electrochromic quality (defined as the maximum contrast achievable). The optimal conditions for electropolymerization in terms of optimum energy consumption and the best electrochromic quality of the films were established.

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Introduction

Since the discovery of conducting polymers 30 years ago [1], changes in their physical properties, such as volume, stored charge, porosity, or color, which are linked to their corresponding oxidation–reduction processes, have found several applications including their use as artificial muscles [2–6], supercapacitors [7], smart membranes [8–12], or electrochromic devices [13–18]. Different material architectures have been developed depending on the desired functionality (thick free standing films for artificial muscles or thin films deposited onto transparent substrates for electrochromic applications). For all these devices to function properly, the constituent materials must be able to undergo redox processes that change their physical properties.

At present, fundamental research into the production and application of electrochromic devices coexists with an increasing amount of market-orientated applications (http://www.gentex.com/, http://www.smartglass.com/, and http://www.saint-gobain-glass.com/exen/index.asp), and after years of research, knowledge of the field is sufficiently mature to encourage large-scale production of these materials and devices.

In this scenario, some aspects that are easily overlooked at laboratory scale, such as energy consumption in the polymerization process or the electropolymerization rate, must be taken into account when large-scale production is being contemplated. Also, the produced materials must meet quality criteria, which reflect the desired functionality:
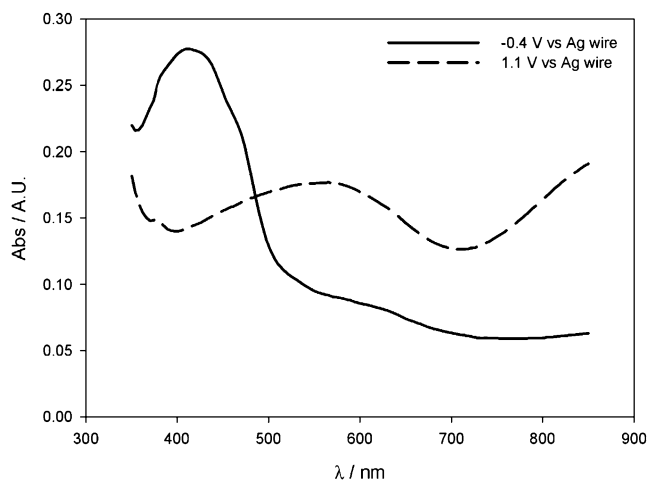
Fig. 1 Visible spectra (350–850 nm) of a PBEDOT-NMCz film in its neutral (−0.4 V vs Ag wire) and oxidized states (1.1 V vs Ag wire). The electropolymerization of the film was carried out at 0.95 V for 6 s in a 1 mM BEDOT-NMCz, 0.1 M LiCF$_3$SO$_3$ acetonitrile solution. The spectra were obtained while submitting the film to 30 s potential steps, at −0.4 and 1.1 V in the background solution

Fig. 3 Polymerization cells containing 1 mM BEDOT-NMCz, 0.1 M LiCF$_3$SO$_3$ acetonitrile solutions after polymerization at 0.75 V (*left*) and after polymerization at 2 V vs Ag wire (*right*)

They should be able to undergo redox processes to provoke the expected changes in properties. In short, large-scale production requires materials that can be produced fast enough to meet demand but that are also of sufficient quality to be used in the desired application.

Electropolymerization is the most widely used method for obtaining conducting polymers due to the ease with which the process can be controlled by means of the imposed current or the applied potential. Compared with other methods, like chemical polymerization or spin-coating, electropolymerization has the benefit of permitting the process to be stopped or the rate to be increased or decreased while maintaining complete control over it. It also allows a better control of the amount of polymerized material because this is directly linked to the charge consumption. Finally, as regards the construction of electro-
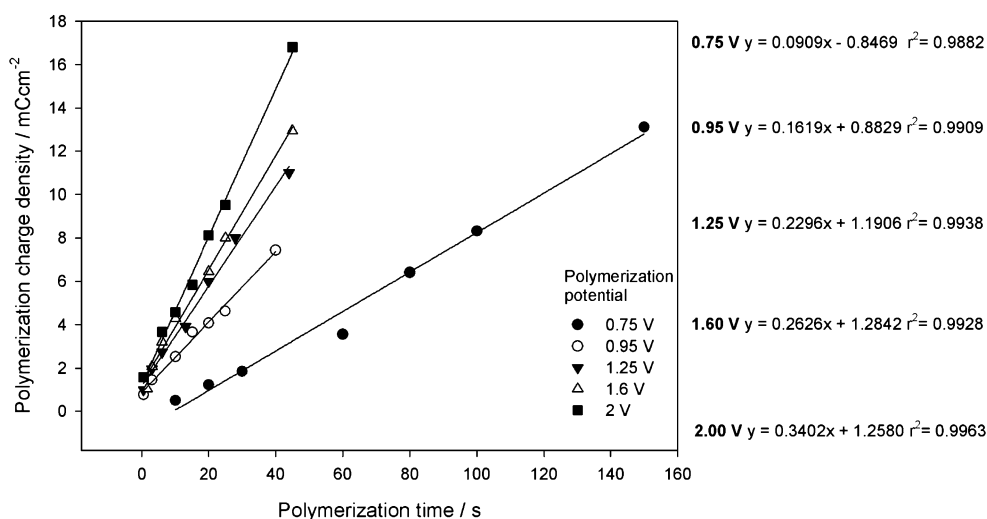
chromic devices, it offers the advantage of directly depositing the polymer onto a convenient surface.

It has been reported that increasing applied potential is translated into an increasing polymerization charge consumed [19–23]. Additionally, it has been reported that as the applied potential increases, parallel reactions consuming extra charge may occur, together with overoxidation and degradation processes [24–27] in the previously deposited polymer leading to a loss in the ability of the material to undergo subsequent redox processes.

The aim of this manuscript is to evaluate the polymerization process of poly [3,6-bis(2-(3,4-ethylenedioxy)

Fig. 2 Evolution of the polymerization charge consumed to generate PBEDOT-NMCz films by potentiostatic polarization at 0.75, 0.95, 1.25, 1.6, and 2 V for different polymerization times. Polymerizations were carried out onto 3.5 cm^2 ITO-coated glass slides in 1 mM BEDOT-NMCz, 0.1 M LiCF$_3$SO$_3$ acetonitrile solutions. The surface area coated by the polymer was 2.1 cm^2 for all the films

0.75 V $y = 0.0909x - 0.8469$ $r^2 = 0.9882$

0.95 V $y = 0.1619x + 0.8829$ $r^2 = 0.9909$

1.25 V $y = 0.2296x + 1.1906$ $r^2 = 0.9938$

1.60 V $y = 0.2626x + 1.2842$ $r^2 = 0.9928$

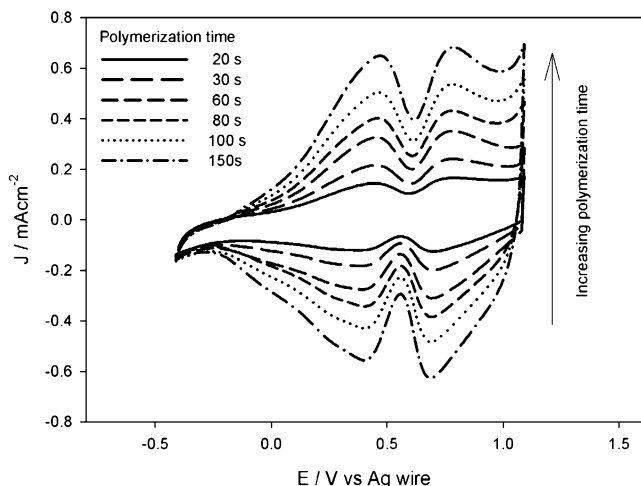**2.00 V** $y = 0.3402x + 1.2580$ $r^2 = 0.9963$

Fig. 4 Control cyclic voltammograms of a series of PBEDOT-NMCz films generated by polarization at 0.75 V for increasing polarization times (20, 30, 60, 80, 100, and 150 s) in 1 mM BEDOT-NMCz, 0.1 M LiCF$_3$SO$_3$ acetonitrile solutions. The voltammograms were carried out in the same monomer-free solution, between −0.4 and 1.1 V at 100 mVs^{-1}

thienyl)-N-methylcarbazole] (PBEDOT-NMCz), in terms of its energetic efficiency and the electrochromic quality (defined as the maximum contrast achievable) of the resulting films. The influence that the polymerization potential and time have on the redox and electrochromic properties of the electrogenerated films was studied.

Experimental

Materials Lithium trifluoromethanesulfonate (LiCF$_3$SO$_3$) from Aldrich was used as received. Acetonitrile (ACROS) was purchased from Fisher scientific and distilled over calcium hydride. An Ag wire pseudo-reference electrode (0.12 V vs normal hydrogen electrode) was used. Indium tin

oxide (ITO)-coated glass slides of nominal resistance R=15–25 Ω and surface area S=3.5 cm^2 were purchased from Delta technologies.

3,6-Bis(2-(3,4-ethylenedioxy)thienyl)-N-methylcarbazole (BEDOT-NMCz) was synthesized as reported earlier [28]. PBEDOT-NMCz is an anodically coloring polymer. It has been used in a complementary way to cathodically coloring polymers like 3,4-polyethylendioxythiophene (PEDOT) or 3,4-propylenedioxythiophene (ProDOT) derivatives [29–31] in dual polymer electrochromic systems. These kinds of system are usually referred to as variable transmission devices because one of their optical states is transparent to visible light (clear state) while the other is partially transmissive (dark state). PBEDOT-NMCz is transparent yellow in its neutral state and is dark blue in its oxidized state. It may take on another intermediate color, lime green, between these two states [28]. Figure 1 shows the visible spectra of PBEDOT-NMCz in its neutral and oxidized states.

Polymerization conditions All electrochemical polymerizations were carried out under constant potential in 1 mM BEDOT-NMCz, and 0.1 M LiCF$_3$SO$_3$ acetonitrile solutions. PBEDOT-NMCz films were obtained at different potentials, namely, 0.75, 0.95, 1.25, 1.6, and 2 V vs Ag wire. The films were polymerized onto ITO-coated glass slides, and all the polymerized films had a surface area of 2.1 cm^2. A stainless-steel sheet with a surface area of 5 cm^2 was use as counter electrode.

Equipment A UV-Vis DINKO spectrophotometer was used for optical characterizations of the films, and an Ecochemie Autolab PGSTAT 100 potentiostat was used for the electrochemical measurements. Polymerization and optical experiments were carried out in cuvette-size glass cells (12×12×45 mm).

Fig. 5 Redox charge densities, obtained by integration of the control voltammograms carried out between −0.4 and 1.1 V, in 0.1 M LiCF$_3$SO$_3$ acetonitrile solutions at 100 mVs^{-1} to those films electrogenerated at 0.75, 0.95, 1.25, 1.6, and 2 V for different polymerization times

0.75 V y = 0.0248x − 0.0712 r^2= 0.998

0.95 V y = 0.038x + 0.376 r^2= 0.9886

1.25 V y = 0.0482x + 0.3253 r^2= 0.9859

1.60 V y = 0.0452x + 0.2739 r^2= 0.9923

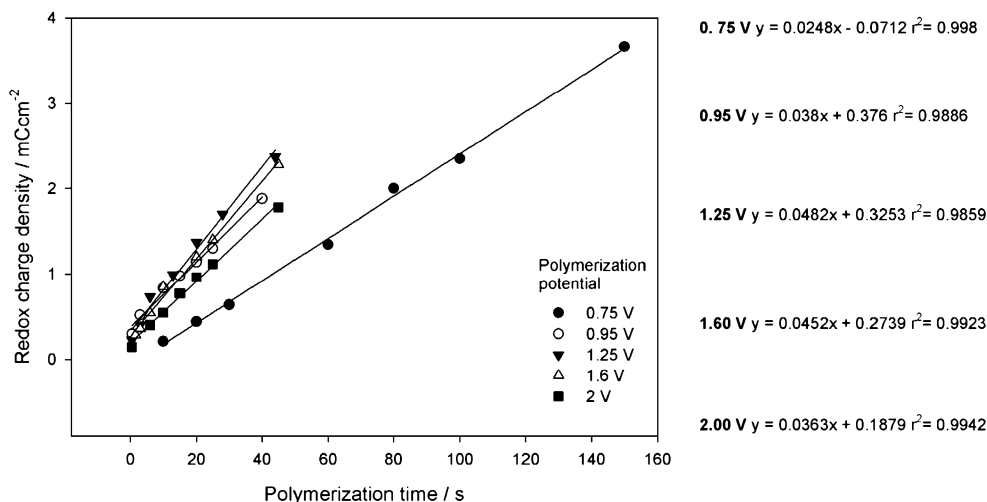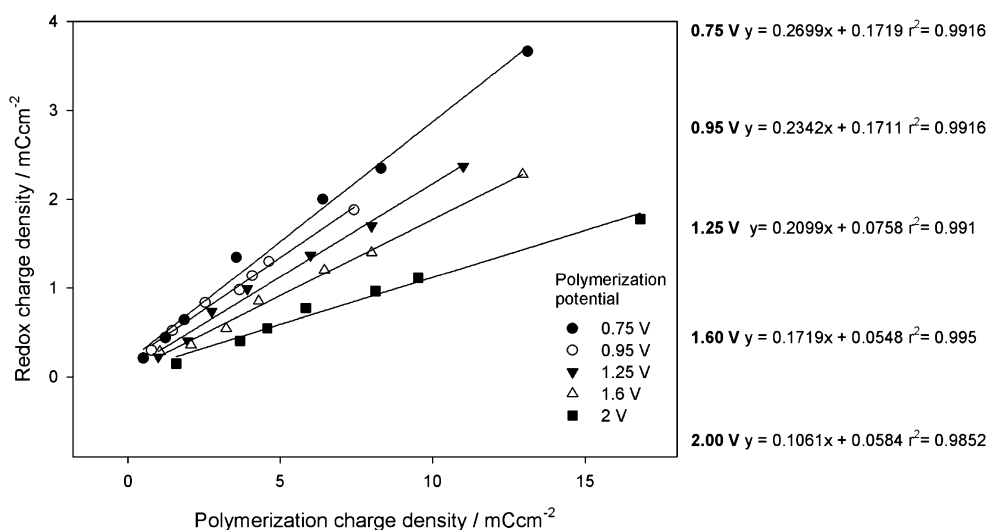**2.00 V** y = 0.0363x + 0.1879 r^2= 0.9942

Fig. 6 Efficiency of the poly-
merization process, defined as
the ratio between redox charge
density of the resulting film and
the charge density consumed
during its polymerization for
PBEDOT-NMCz films electro-
generated at different potentials

0.75 V $y = 0.2699x + 0.1719$ $r^2 = 0.9916$

0.95 V $y = 0.2342x + 0.1711$ $r^2 = 0.9916$

1.25 V $y = 0.2099x + 0.0758$ $r^2 = 0.991$

1.60 V $y = 0.1719x + 0.0548$ $r^2 = 0.995$

2.00 V $y = 0.1061x + 0.0584$ $r^2 = 0.9852$

Results and discussion

Electrochemical characterization

Electropolymerization Films of PBEDOT-NMCz were de-
posited onto ITO-coated slides at 0.75, 0.95, 1.25, 1.6 and
2 V vs Ag wire for different polymerization times, and the
charge consumed was registered. The evolution of the
charge consumed as a function of polymerization time for
each applied potential series is shown in Fig. 2. Linear
relations were found for each potential. It can be observed
that increasing applied potential leads to increasing charge
consumption.

While carrying out the experimental procedure, it was
observed that polymerization potentials higher than 1.25 V
and long polymerization times led to the appearance of a
dark cloud over the ITO surface. When this occurred, the
polymerization was stopped. This in-solution polymeriza-
tion without deposition of the polymer has been explained
by changes in the chemical environment of the solution:

High polymerization rates promote the release of a great
number of protons, increasing the acidity of the medium
and promoting chemical polymerization of the monomer
[21, 32]. Differences between polymerization solutions
with and without the appearance of this dark cloud are
shown in Fig. 3.

Redox characterization After polymerization, every film
was cycled in a 0.1 M $LiCF_3SO_3$ monomer-free acetonitrile
solution, between −0.4 and 1.1 V, at 100 mVs^{-1}. Figure 4
shows the cyclic voltammograms obtained for the films
polymerized at 0.75 V.

The charge density involved in the oxidation (or
reduction) of the polymer films was determined by
integrating the anodic (or cathodic) branch of the control
voltammogram and dividing by the film surface area. This
was defined as the redox charge density for the studied
film. As expected, the redox charge density increased for
increasing polymerization times at a constant polymeriza-
tion potential. A linear increase of the redox charge density

Fig. 7 a Power consumption
during the polymerization, **b**
redox site production rate, and **c**
efficiency of the polymerization
process for PBEDOT-NMCz
films electrogenerated at differ-
ent potentials. The redox charge
densities of the resulting films
were obtained by integration of
control voltammograms between
−0.4 and 1.1 V vs Ag wire.
Efficiency of the polymerization
process was defined as the ratio
between the redox charge den-
sity of a film and charge density
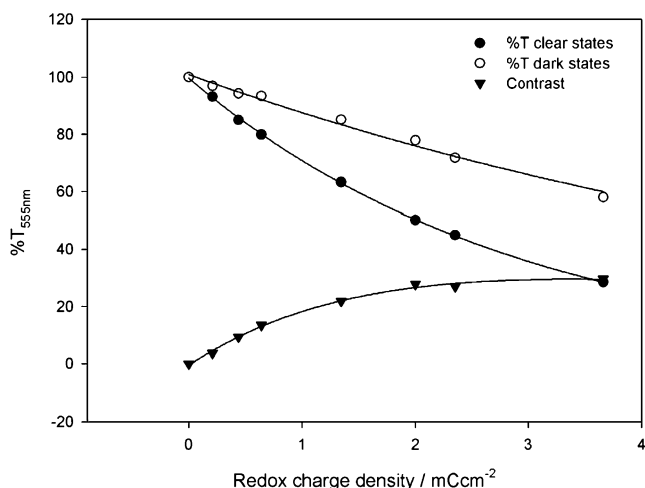consumed during its polymeri-
zation process
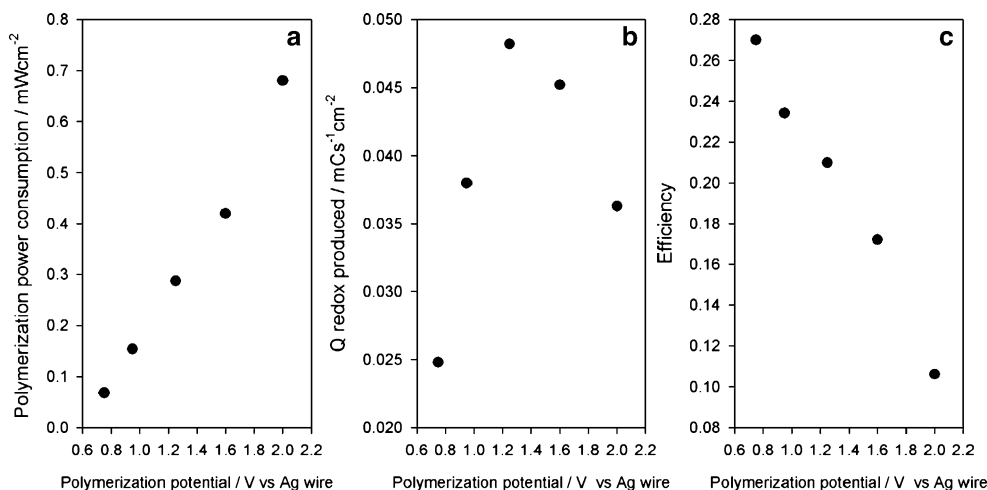
Fig. 8 Transmittances at 555 nm for the clear and dark states of PBEDOT-NMCz films as a function of their redox charge density. Films were polymerized at 0.75 V, and the redox charge densities were obtained from control voltammograms between −0.4 and 1.1 V vs Ag wire. Transmittances were obtained by submitting the films to potential steps between −0.4 and 1.1 V vs Ag wire. *Dots* show experimental values while *lines* are the exponential decay fittings, according to Eq. 1

of the films vs polymerization time was observed for every studied potential (Fig. 5). Slopes of the depicted plots determine the redox site production rate, that is, the redox charge density of a film divided by its polymerization time. They were found to rise for increasing polymerization potentials, reaching a maximum when the polymerization potential was 1.25 V and then decreasing. The maximum and the subsequent diminution could be explained by overoxidation and degradation processes: At high anodic potentials, the generation of radicals by simultaneous oxidation of the solvent promotes chemical attack on the deposited polymer, breaking the conjugation and subsequently diminishing the electroactivity of the resulting film [33].

Efficiency of the process Polymerization efficiency was defined as the ratio between redox charge density of the obtained film and polymerization charge density consumed

to generate the film. A continuous decrease of the polymerization efficiency for increasing potentials of polymerization was found (Fig. 6).

The results obtained for the electrochemical characterization are summarized in Fig. 7. Figure 7a shows the polymerization charge multiplied by the applied potential, giving the electrical power consumption as a function of the applied polymerization potential. The consumed power increases for increasing potentials of polymerization. Figure 7b shows the rate at which redox sites were created per second of polymerization as a function of the polymerization potential. The maximum rate was obtained at 1.25 V. Figure 7c shows the efficiency of the polymerization processes, which steadily decreased as the polymerization potentials increased, meaning that more energy was being consumed in the polymerization process to get the same results in terms of redox charge density.

It seems then that the redox site production rate can be increased in the potential range from 0.75 to 1.25 V, although such an increase will be accompanied by higher energy consumption. In terms of industrial scale processes, this means that by increasing polymerization potential in that range, production can be speeded up. These findings will be useful for establishing a balance between speed of production and associated increased energy consumption (and therefore cost of the production).

Optical characterization

The Beer–Lambert law relates absorbance of a material to the concentration of absorbing species and thickness and is expressed as:

$$A = \varepsilon c l \qquad (1)$$

where ε is the molar absorption coefficient, c the volume concentration of absorbing species, and l the thickness of the material. The assumptions made are: (a) the concentration of the absorbent species is uniform, and (b) the

Table 1 Experimental fitting parameters for the equation %T=100exp($-\eta q$), relating transmittance and redox charge density for an electrochromic material

Polymerization potential/V vs Ag wire	Clear states			Dark states		
	a	b	r^2	a	b	r^2
0.75	101.39	0.1462	0.9898	99.657	0.3417	0.9999
0.95	100.08	0.1624	0.9874	99.113	0.3547	0.9912
1.25	98.912	0.1344	0.9878	94.505	0.2829	0.9854
1.6	100.45	0.2223	0.9953	95.715	0.3084	0.9889
2	101.39	0.2616	0.9877	98.475	0.3126	0.9877

a corresponds to the 100 theoretical values, while *b* to the η values. Relations were obtained for PBEDOT-NMCZ films and their transmittance on clear and dark states (555 nm). r^2 corresponds to correlation coefficient.

concentration is sufficiently low for there to be no more than one absorbing species along the perpendicular direction at each point. As long as these assumptions are true, the absorbance of a single surface with the same total amount of absorbent species will be equivalent. Therefore Eq. 1 can be expressed as $A=\varepsilon'c_s$, with c_s the total number of absorbent species present in the material divided by its surface, and $\varepsilon'=\varepsilon N_A$ (N_A=Avogadro's constant). Considering that the creation and elimination of absorbent species is proportional to the redox charge consumption [34], the final expression for the absorbance will be:

$$A = \eta_a q \qquad (2)$$

where q is the redox charge consumed per unit area (charge density), and η_a corresponds to coloration efficiency, defined as the charge density q consumed per unit of absorbance change. Consequently, transmittance can be expressed as $T=\exp(-\eta q)$, with $\eta=2.303\eta_a$, or

$$\%T = 100\exp\left(-\eta q\right) \qquad (3)$$

Considering that the contrast (ΔT) of an electrochromic material is defined as the difference between percent transmittance in its clear and dark states, then

$$\Delta T = 100(\exp\left(-\eta_c q\right) - \exp\left(-\eta_d q\right)) \qquad (4)$$

with η_c and η_d being the coloration efficiencies for clear and dark states, respectively.

This mathematical expression can be used to obtain the maximum contrast achievable for that material as a function of its redox charge density, simply by making $d\Delta T/dq=0$ [35].

This procedure was used to characterize all the polymerized films, thus obtaining the maximum contrast achievable for every series and therefore providing a measurement of their electrochromic quality as a function of the polymerization potential.

Each polymer film was submitted to potential steps between −0.4 and 1.1 V, and the transmittance at 555 nm was recorded. Figure 8 shows the exponential relations obtained from the films electrogenerated at 0.75 V. Table 1 shows the fitted parameters (according to Eq. 3) obtained for all the series of films electrogenerated at different potentials.

From the fitting parameters shown in Table 1 and according to Eq. 4, the evolution of the contrast as a function of the redox charge density of the films was obtained for each series; these evolutions are plotted in Fig. 9. The maximum contrast for the different series, together with the redox charge density of the corresponding film, was calculated and is shown in Table 2. The electrochromic quality of the films polymerized at 0.75, 0.95, and 1.25 V remained the same, but the contrast decreased for films electrogenerated at 1.6 and 2 V, a decrease that can be attributed to the presence of overoxidation processes at high anodic potentials of polarization. As a consequence, thicker
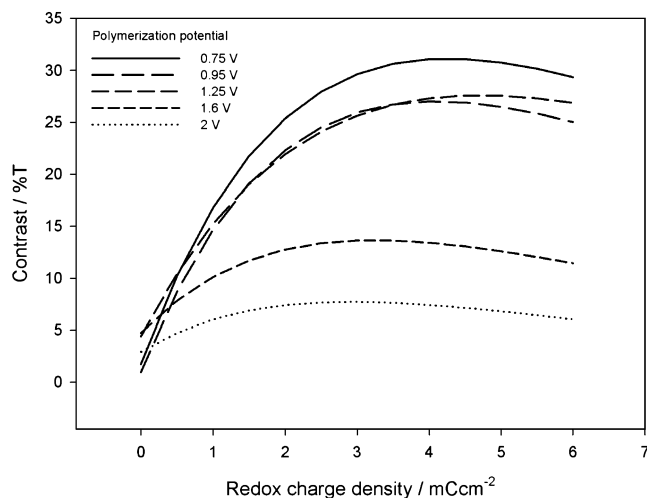

Fig. 9 Evolution of the optical contrast as a function of redox charge density for PBEDOT-NMCz films polymerized at different potentials (0.75, 0.95, 1.25, 1.6, and 2 V)

films were generated with lower electroactivity, that is, a lower proportion of redox sites along the polymer chain. Optically, this is translated into a certain amount of material that does not contribute to the electrochromic change but does contribute to the absorption of the material, thus lowering the final contrast achievable.

Optimization of the production process

With regards to large-scale production criteria, which must take into account the energy consumption, the speed of production, and the quality of the resulting films, several remarks can be made. The simplest way to increase the rate of polymer production is to increase the applied potential, there being a potential range where the production rate of redox sites increases with the potential (0.75 to 1.25 V vs Ag wire for the studied polymer), and the electrochromic quality of the films is maintained. However, any increase in polymerization potential will translate into higher energy consumption, which will affect the final cost of the product.

Higher anodic potentials of polymerization (1.25 to 2 V vs Ag wire for the studied polymer) lead to a drop in redox site

Table 2 Values of maximum contrast achievable and the redox charge density associated for PBEDOT-NMCz films polymerized at different potentials

Polymerization potential (V vs Ag wire)	Redox charge density for maximum contrast (mCcm^{-2})	Maximum contrast	%T clear state	%T dark state
0.75	4.23	30.68	54.18	23.5
0.95	4.01	28.28	52.17	23.88
1.25	4.7	27.59	52.56	24.97
1.6	3.24	13.64	48.87	35.22
2	2.92	7.71	47.23	39.52

production, resulting in a more inefficient process, due to parallel reactions of polymeric degradation (overoxidation). This will be reflected in lower electrochromic quality films.

The experimental procedure described in this study has been used to determine the potential range where the polymerization rate can be maximized without compromising the optical quality of the films.

Conclusions

Films of PBEDOT-NMCz, an electrochromic polymer often used as complementary to cathodically coloring films, were polymerized at different potentials. The resulting films were electrochemically and optically characterized. The charge consumed during polymerization, the number of redox sites created, and the efficiency of the polymerization process (defined as the charge consumed to create one redox site) were determined for the studied potentials of polymerization. The electrochromic quality (defined as the maximum contrast achievable) of the resulting films was measured.

Optimization of the production process was discussed from a large-scale production point of view, it being found that the optimum potential range of polymerization, where the production rate can be increased without losing electrochromic quality of the resulting films, ranges from 0.75 to 1.25 V. Polymerization at higher potentials produces films of poor electrochromic quality.

References

1. Chiang CK, Fincher CR, Park YW, Heeger AJ, Shirakawa H, Louis EJ, Gau SC, MacDiarmid AG (1977) Phys Rev Lett 39:1098
2. Smela E (2003) Adv Mater 15:481
3. Kaneto K, Kaneko M, Min Y, MacDiarmid AG (1995) Synth Met 71:2211
4. Bay L, West K, Sommer-Larsen P, Skaarup S, Benslimane M (2003) Adv Mater 15:310
5. Baughman RH (1996) Synth Met 78:339
6. Otero TF, Angulo E, Rodriguez J, Santamaria C (1992) J Electroanal Chem 341:369
7. An KH, Jeon KK, Heo JK, Lim SC, Bae DJ, Lee YH (2002) J Electrochem Soc 149:A1058
8. Price WE, Too CO, Wallace GG, Zhou D (1999) Synth Met 102:1338
9. Partridge AC (1995) Electrochim Acta 40:1199
10. Otero TF, Ariza MJ (2003) J Phys Chem B 107:13954
11. Ehrenbeck C, Juttner K (1996) Electrochim Acta 41:1815
12. Ehrenbeck C, Juttner K (1996) Electrochim Acta 41:511
13. Argun AA, Aubert PH, Thompson BC, Schwendeman I, Gaupp CL, Hwang J, Pinto NJ, Tanner DB, MacDiarmid AG, Reynolds JR (2004) Chem Mater 16:4401
14. Granqvist CG (2000) Sol Energy Mater Sol Cells 60:201
15. Hyodo K (1994) Electrochim Acta 39:265
16. Mortimer RJ (1999) Electrochim Acta 44:2971
17. Rosseinsky DR, Mortimer RJ (2001) Adv Mater 13:783
18. Somani PR, Radhakrishnan S (2003) Mater Chem Phys 77:117
19. Otero TF, Santamaria C (1991) J Electroanal Chem 312:285
20. Otero TF, Santamaria C (1992) Synth Met 51:313
21. Otero TF, Rodriguez J (1993) Synth Met 55:1418
22. Kaplin DA, Qutubuddin S (1995) Polymer 36:1275
23. Du X, Wang Z (2003) Electrochim Acta 48:1713
24. Schlenoff JB, Xu H (1992) J Electrochem Soc 139:2397
25. Pigani L, Heras A, Colina A, Seeber R, Lopez-Palacios J (2004) Electrochem Commun 6:1192
26. Barsch U, Beck F (1996) Electrochim Acta 41:1761
27. Christensen PA, Hamnett A (1991) Electrochim Acta 36:1263
28. Sotzing GA, Reddinger JL, Katritzky AR, Soloducho J, Musgrave R, Reynolds JR (1997) Chem Mater 9:1578
29. Sapp SA, Sotzing GA, Reynolds JR (1998) Chem Mater 10:2101
30. Schwendeman I, Hickman R, Sonmez G, Schottland P, Zong K, Welsh DM, Reynolds JR (2002) Chem Mater 14:3118
31. Sapp SA, Sotzing GA, Reddinger JL, Reynolds JR (1996) Adv Mater 8:808
32. Izutsu K (2002) Electrochemistry in nonaqueous solutions. Wiley-VCH, Weinheim
33. Rodriguez J, Grande HJ, Otero TF (1997) Polypyrroles: from basic research to technological applications. In: Nalwa HS (ed) Handbook of organic conductive molecules and polymers, vol 2. Wiley, New York
34. Monk PMS, Mortimer RJ, Rosseinsky DR (1995) Electrochromism: fundamentals and applications. VCH, Weinheim
35. Lim JY, Ko HC, Lee H (2005) Synth Met 155:595