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Electroanalytical features of non-uniformly doped conducting poly-3-(3,4,5-trifluorophenyl)thiophene films

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Specially prepared, thin poly-3-(3,4,5-trifluorophenyl)thiophene, PTFPT, films were shown to possess stable p- and, most importantly, n-doping in TEABF₄/sulfolane (SF) solutions. Electrodes comprising PTFPT films were studied by cyclic voltammetry (CV), potentiostatic intermittent titration (PITT), and electrochemical impedance spectroscopy (EIS). A detailed analysis of the shape of the time-dependent current transients during PITT characterization of the PTFPT electrodes has been performed. The non-uniform character of the PTFPT film doping was proved. Plots of dlog|I(t)|/dlog t vs. t/τ_d were found to be useful for understanding the response of potentiostatic transients. The Cottrell time domain during potentiostatic transients was found to be very narrow, reflecting the drastic effect of the Ohmic potential drops (mainly across the film's bulk) on the semi-infinite diffusion current transient at the shortest times, and a wide distribution of the diffusion time constants. PITT and EIS characterizations provided converging results with respect to the relevant diffusion time constants and the non-uniform character of PTFPT film doping in the SF solution. EIS measurements were found to be very useful for the determination of diffusion time constants, as they allow more effective separation of the medium frequency, Warburg response from the Ohmic and the kinetic high-frequency responses.

Introduction

Practical applications of electronically conducting polymers (CP) in LED devices, electrochemical transistors, electrochromic windows, and rechargeable batteries are largely based on the phenomenon of reversible p- and n-doping.¹⁻⁶ By definition, simple p-doping is the removal of electrons from the π -conjugated polymeric backbone (partial oxidation), which is equivalent to the creation of a cation-radical species. The latter is stabilized both by delocalization within the π -system, and by anion insertion from the solution. N-doping (in its simple form, without the participation of co-ions) by the same principle is the partial reduction of the π -system with the formation of anion-radicals, stabilized by cations coming from the solution. Only a few CP among them, i.e., polyacetylene,⁷ poly-*p*-phenylene,⁸ and polythiophene,⁹ can be doped in both directions. As a rule, repeated and stable n-doping/ neutralization of these polymers is much more difficult to obtain, compared to p-doping. For example, numerous attempts to increase the n-doping level of underivatized polythiophene were not very successful: although the variation of the solvent and electrolyte nature allowed this level to increase to a certain extent, it was never as high as that of the p-doping (see a comprehensive review¹⁰).

An important advantage of CP over conventional inorganic ion-insertion cathodes and anodes for rechargeable batteries is that a simple chemical derivatization of the CP structure may lead to a drastic, targeted change of their unique molecular properties.¹ In order to balance the n- and p-doping levels, a series of monomers based on (fluorophenyl) thiophenes has been suggested and tested in experimental cells.^{11–13}

In the present work, we obtained 3-(3,4,5-trifluorophenyl)thiophene by modifying the synthetic procedure reported in ref. 11. Further electropolymerization of this monomer resulted in thin poly-3-(3,4,5-trifluorophenyl)thiophene, PTFPT films that showed a relatively high n-doping level.

The goal of the present work was to rigorously measure and characterize the potential dependencies of the major equilibrium and kinetic parameters related to n- and p-doped PTFPT film: the differential intercalation capacitance, C_{dif} and the chemical diffusion coefficient, D_i , respectively. These were obtained by the combined application of cyclic voltammetry (CV), potentiostatic intermittent titration (PITT), and electrochemical impedance spectroscopy (EIS). The experimental results attained were then treated using classical finite-space diffusion models, from which a major feature of the electrochemical doping of the PTFPT electrodes, namely, the films' nonuniformity (heterogeneity), was envisaged. We then examined how this heterogeneity was specifically reflected in different kinds of electroanalytical measurements. This is expected to contribute to a better application of these techniques for quantitative characterization of highly heterogeneous electrochemical systems.

Experimental

Synthesis of the monomer

3-(3,4,5-trifluorophenyl)thiophene was obtained by a modification of the reported procedure¹¹ related to the palladium catalyzed coupling reaction of a zinc complex of trifluorobenzene with 3-bromothiophene. Either dichlorobis(triphenylphosphine) palladium(II) or tetrakis(triphenylphosphine) palladium(0) can be used as a catalyst. However, the yield was better with the former. The reaction was carried out in dry THF under Ar atmosphere. The final product contained about 5% of a 3,4,5,-3',4',5'-hexafluoro-biphenyl by-product, which, however, did not affect the subsequent electropolymerization of 3-(3,4,5-trifluorophenyl)thiophene. The analytically pure 3-(3,4,5-trifluorophenyl)thiophene can, however, be obtained by the low-temperature precipitation of the biphenyl by-product from hexane.

Techniques and equipment

PTFPT films were deposited potentiostatically on Pt wires $(\emptyset 0.5 \text{ mm}, \text{ geometric surface area of } 0.11 \text{ cm}^2)$. Pt wire pre-treatment, as well as the construction of two electrochemical cells used in this work for electropolymerization and electroanalytical characterization in a monomer-free solution, was the same as that previously described for polypyrrole films.¹⁴ For the electropolymerization, the counterelectrode was a Pt grid, whereas a reversible Ag/0.1 M AgNO₃ in 0.25 M TEABF₄/acetonitrile (AN) separated by a glass frit from the working compartment served as the reference electrode. This compartment was filled with 0.25 M TEABF₄ in AN + 0.05 M 3-(3,4,5-trifluorophenyl)thiophene. Immediately after electropolymerization, the doped film was neutralized by a linear potentiodynamic scan in the same monomer-containing solution. The Pt electrode with the deposited film was then removed from the cell, rinsed several times with pure AN, and, finally, with the solvent in which the doping process was studied. The film's electrode was then inserted into an undivided 3-electrode cell for CV, PITT and EIS characterization. In this cell, the WE wire with the deposited film was surrounded by a counterelectrode (Pt cylinder). The reference electrode was either a Li or an Ag wire in a thin plastic tube located in the vicinity of the working electrode. Li was used as a quasi-reference electrode in PC14,15 and SF,16 whereas Ag wire was used in AN. We monitored the potential of the Li wire in the above solvents and found it to be -3.65 and -3.67 V, respectively, using a standard Fc/Fc⁺ electrode. Measurements over a period of one day showed that the shift in the potential was negligible, about several mV. Hence, the use of this RE is fully justified, based on the stability measurements and previous experience.

All measurements and manipulations were performed in a glove box at room temperature, under highly pure Ar atmosphere. The oxygen and water content did not exceed several ppm. TEABF₄ was battery grade from Tomiyama. The residual water content in the dry solutions did not exceed 20 ppm, as follows from Karl Fischer titrations.

CV, PITT, and EIS measurements were performed using Autolab/PGSTAT20 potentiostat/galvanostat systems containing FRA modules driven by Pentium II personal computers using GPES software from Eco Chemie (Utrecht, The Netherlands). CV was performed in a staircase mode with potential steps of 0.3 mV at a scan rate of 50 mV s⁻¹.

PITT characterizations of the PTFPT electrodes were performed as follows. The first potentiostatic titration of the films was performed during the p-doping (oxidation of neutral film), followed by the subsequent p-undoping (reduction of the oxidized films). Then the potentiostatic titration was similarly repeated for the n-doping (reduction of neutral films) and the subsequent n-undoping (oxidation of the reduced film). In each step the current was recorded for approximately 5 min. At the end of each step, at moderate doping levels, the current dropped below $2 \,\mu A \, \text{cm}^{-2}$. It was assumed that at this condition complete equilibrium is maintained within the films. Then the next potential step was applied. In the limit of high doping levels, the current reached a time-independent, background value of 5 μ A cm⁻², which was subtracted from the measured values. The PITT data were first analyzed with the use of finite-space diffusion models for homogeneous intercalation electrodes.^{17,18} The pronounced deviation of the behavior of the p- and n-doped PTFPT film from that predicted by the finite-space diffusion models was observed for a wide time domain, with the use of appropriate characteristic currenttime plots.

EIS was performed at several potentials under constant potential polarization. Before measurements, the PTFPT film was preliminary polarized at the related potential for 10 min. The amplitude of the ac voltage used was 5 mV. The frequency range measured extended from 374 kHz to 50 mHz.

Results and discussion

PTFPT films were deposited on Pt wires, as described above. The polymerization potential of 1.39 V was chosen to ensure an optimal condition for growth of the polymer films (see Fig. 1a). A moderate increase in the current after a delay of more than 10 s corresponded to appearance of the polymer nuclei on the current collector surface (the related surface area increases) and further growing of the polymer coating. When the charge passed, Q_{polym} , reached the value of 25 mC, the polarization was turned off. The film was neutralized in the same solution in a potentiodynamic scan from 0.85 to 0 V at a scan rate of 50 mV s^{-1} (see Fig. 1b). The neutralization (undoping) of the oxidized film, as is seen from this figure, is reflected by a characteristic peak at around 0.55 V; the corresponding charge, Q_{neut} , was equal to 2.5 mC. The maximal doping level, x, was evaluated from the ratio of the neutralization to polymerization charge, taking into account the known stoichiometry of the polymerization reaction¹¹⁻¹³ and assuming a Faradaic efficiency of 100%: x/ $(2+x) = Q_{\text{neut}}/Q_{\text{polym}}$, from which $x = 0.22 \text{ e}^-$ per moiety unit $(e(\text{mu})^{-1})$ was found. The high Faradaic efficiency estimated for these reactions under the specified conditions is a reasonable assumption that can be separately checked, e.g., by weighing the films deposited onto massive current collectors (as was the case in the previous work¹³). The above value of x coincides well with those reported earlier for PTFPT films,11-13 and was not very different from that usually obtained with pristine p-doped polythiophene.

Note that the specified polymerization potential for electrosynthesis of PTFPT films was chosen in order to maintain sufficient rates of the films' growth. A decrease in the



Fig. 1 I vs. time curves for the potentiostatic synthesis of a PTFPT film (a) and its neutralization under potentiodynamic conditions (b) in a 0.25 M TEABF₄/AN + 0.05 M (3,4,5)TFPT solution.

polymerization potential with the corresponding increase in the deposition time (to keep the same charge) resulted in poor films, which were capable of p-doping but could not reach a substantial n-doping level.

We estimated the film's thickness as 0.6 μ m using a commonly used method, namely, comparing the amount of charge passed during the electropolymerization of the PTFPT films with the charge required to prepare reference films of known thickness, as previously reported.¹¹

As-neutralized PTFPT films were immersed in monomerfree, 0.25 M TEABF₄ solutions in either acetonitrile (AN), propylene carbonate (PC), or sulfolane (SF). CV curves measured with PTFPT electrodes at a scan rate of 50 mV s⁻¹ in each of these three non-aqueous solutions, during both p- and n-doping, are depicted in Fig. 2. It is seen that the CV responses from the n-doped film are qualitatively similar to those for the p-doped polymer. When analyzing the dependence of the related peak-potential separations on the solvent nature, the reversibility of both p- and n-doping processes tends to increases in the SF \ll PC < AN sequence. Note that during p-doping the films exhibited approximately the same redox-charge, independent of the solvent nature, with relatively high Faradaic efficiencies (92–94%).

The curves shown in Fig. 2 correspond to the stable CV responses attained during consecutive cycling of the freshly prepared films for different periods of time. Whereas only a few cycles were necessary to reach the steady-state response in AN and PC, more than 30 cycles were required to obtain such a response in a SF-based solution. We thus suspected that poorer kinetics of the p- and n-doping of PTFPT films in the latter solution might be connected with the films' slow impregnation by the SF-based solution. A similar gradual increase of the redox-charge related to the SF based solutions, and its lower absolute value compared to that in PC-based solutions was recently reported for poly(vinylferrocene) (PVF) film electrodes.¹⁹

The assumption about the important role of swelling in the film's redox kinetics was further checked using EIS and PITT. CV, as a large-amplitude technique, could provide only gross features of the kinetics of p- and n-doping of PTFPT electrodes, reflected mainly by the value of the peak-potential separation. Small amplitude techniques, such as PITT and EIS, were applied in this work in parallel, in order to study the kinetics of the PTFPT electrodes as a function of both time (frequency) and equilibrium potential (doping level).



Fig. 2 Stable (steady-state) CV curves measured with (the same or similar) PTFPT film(s) of *ca.* 0.6 μ m thick (prepared in an AN solution), which was p- and n-doped in SF, PC, and AN. Scan rate and the solution compositions are indicated. For comparison, a CV curve measured in an AN *vs.* Ag quasi-reference electrode is presented *vs.* a Li electrode by shifting the potential by 3.32 V towards more positive values.

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However, meaningful PITT and EIS characterizations are only possible with insertion electrodes possessing long-term stability (cyclability). Although as-prepared PTFPT films showed more facile kinetics in AN and PC solutions compared to that in SF, their charge and discharge capacities (mainly, for n-doped films) deteriorated rapidly with the number of cycles (or polarization time) in the former two solutions. In contrast, despite the clearly poorer doping kinetics of PTFPT films in SF solutions, long-term stability of the film, especially for the n-doped film, was rather good. At the end of the PITT and EIS characterizations, PTFPT electrodes usually lost 14 and 28% of their initial redox-charge during the p- and ndoping, respectively. Interestingly, the Faradaic efficiency of the n-doping of the PTFPT electrodes increased in the AN < PC < SF sequence: 83, 88, and 91%, respectively, i.e., in the reverse order with respect to the rate of the films' doping in these three solvents. Thus, the detailed electroanalytical characterizations of PTFPT could be performed in SF, as only this solvent enabled the required long-term stability of the electrodes.

The solid lines in Figs. 3a and b reflect stable, steady-state, voltammetric responses of the film during its repeated p- and n-doping, respectively. However, for the sake of comparison with the results obtained from PITT, the voltammetric curves in these figures were normalized by the scan rate. In such a way, the calculated quantity presents the so-called differential capacitance of the doping/undoping process in terms of CV: $C_{\text{dif}} = I_{\text{cv}}/\nu$. Here, I_{cv} stands for the voltammetric current, and ν for the scan rate.

In order to determine the dependence of D_i on the electrode's potential using PITT, the current-time response for each potential step should be treated in terms of the two quantities:²⁰ The first one is the differential (incremental)



Fig. 3 Comparison of the plots of the differential capacity, C_{dif} . *vs.* potential, *E*, obtained by CV (solid lines) and PITT (dotted lines) during p- and n-doping (a and b, respectively).

capacity C_{dif} , defined as the ratio of the charge injected during the whole potential step (ΔQ) to the width of this potential increment (ΔE):

$$C_{\rm dif} = \Delta Q / \Delta E, \tag{1}$$

where ΔQ can be obtained by numerical integration of the related I vs. t curve. The C_{dif} quantity is an important equilibrium characteristic of the doped (undoped) film. The dependencies of C_{dif} on the potential are shown in Figs. 3a and b for the p- and for the n-doping, respectively. Comparing the plots of C_{dif} vs. potential (E) obtained from PITT and from CV (see Figs. 3a and b) shows that the former technique basically provides a closer approach to equilibrium state of the film compared to the latter technique. The reason for this is that the characteristic accessible time window of the CV curves measured at the scan rate of 50 mV s^{-1} appears to be considerably less than that for the PITT measurements (by approximately 6-fold). Ohmic potential drops, bulk film resistance, and slow interfacial and diffusion kinetics will broaden the CV curves measured (unless the potential scan rate is very slow), whereas all these factors become insignificant when current transients during PITT are integrated over a sufficiently long period of time. There is one shortcoming of PITT compared to CV: The CV curves shown in Fig. 3 were measured in a stepped mode with a potential height of 0.3 mV. Thus the number of points corresponding to the half-peak width exceeded 1300. In the PITT experiment, we usually performed 8 titrations, 50 mV each step. Hence, the $C_{\rm dif}$ curve contained 8 points. A further increase in the number of experimental points in the PITT experiments by reducing potential step height, would lead to less accurate values of $C_{\rm dif}$ calculated from each step. This is because the incremental charge due to doping becomes comparable with the parasitic charge consumed by inevitable background reactions, which should be normally subtracted from the total measured charge. On the other side, increasing the number of experimental points (C_{dif}) measured accurately, require a decrease in titration time for each step; thus, the measured response may deviate from the true, equilibrium value.

Once C_{int} was found, further calculation of D_i by PITT required the determination of the characteristic kinetic para-meter $It^{1/2}$ for each of the potential steps. Earlier, we proposed treating the experimental PITT data related to the intercalation electrodes, using $It^{1/2}$ vs. log t plots (see ref. 20 and references therein). This was helpful for the following reasons: (i) The plot visualizes the separation between a short-time (Cottrell) domain, and a portion of the plot, related to finite-space diffusion. A combination of the two parameters, C_{int} and $H_{\text{Cottrell}}^{1/2}$ defines the related diffusion time constant $\tau_d(E)$.²⁰ (ii) The normalized $H^{1/2}/H_{\text{Cottrell}}^{1/2}$ vs. log t plot obtained for a variety of equilibrium potentials possesses a remarkable property of congruency (for a homogeneous film): the shape of the curve is invariant with respect to $\tau_d(E)$.²¹ Deviation of the shape of the experimental curves from the theoretical ones may clearly reflect non-uniformity of the redox films.^{21,22} In an ideal case, i.e., in the absence of Ohmic and kinetic limitations, the Cottrell region appears in the $It^{1/2}$ vs. log t plot as a horizontal straight line.²⁰ If, on the contrary, Ohmic and kinetic limitations considerably affect the short-time current response, the Cottrell domain, *i.e.*, $It^{1/2}$ vs. t or log t appears as a function with maximum or minimum, depending on the sign of the current.20

Fig. 4a shows a typical example of an $It^{1/2}$ vs. log t plot obtained from PITT measurements during n-doping of a PTFPT electrode (a potential step from 1.55 to 1.50 V). The ordinate value at the minimum, *i.e.*, at log t = -0.222 s, was taken as the $It_{Cottrell}^{1/2}$ value, from which the diffusion time can be calculated. Deviation of $It^{1/2}$ from the $It_{Cottrell}^{1/2}$ at longer times is caused by finite-space diffusion, whereas deviation of $It^{1/2}$ from the $It_{Cottrell}^{1/2}$ at shorter times is mainly due to Ohmic potential drops (in the solution and in the bulk of the film, especially, in its neutral state) and kinetic limitations (for a detailed analysis of the latter case, see recent paper by Montella²³).



Fig. 4 Current response obtained from the PTFPT film in the SF solution during its n-doping from 1.55 to 1.50 V (vs. Li), treated in different plots: $It^{1/2}$ vs. log t (a), I vs. $t^{-1/2}$ (b), log|I| vs. t (c), and log|I(t)|/dlog t vs. t/τ_d (d).

An important feature of the curve shown in Fig. 4a is that, along with the main peak falling on the short-time domain, one can clearly see a portion of the curve of a relatively small slope in the time domain from 50 to 125 s. An ideal uniform film should have only one Cottrell domain (*i.e.*, a single value of τ_d), and thus the above inflection on the $It^{1/2}$ vs. log t curve implies a secondary, less expressed Cottrell domain. It can be formally related to a higher value of τ_d due to the film's non-uniformity.²¹ This non-uniformity may originate from either a distribution of CP fibrils thickness (although D_i remains the same), or, alternatively, from a distribution of D_i due to the different extent of swelling of different parts of the PTFPT film. The latter factor of the film's non-uniformity seems to be in line with the relatively slow kinetics of its swelling in the SF solution, as verified by CV. Note that the shape of the $It^{1/2}$ vs. log t curve (i.e., the presence of a major and a secondary Cottrell domain) was qualitatively independent of the equilibrium potential of the film (or the related doping level). This latter observation substantiates, as a first approximation, the use of finite-space diffusion models (elaborated for uniform intercalation electrodes)^{17,18} for the determination of τ_d related to a specific, particular domain of the nonuniform intercalation electrode.

The potential dependence of τ_d related to the short time Cottrell domains of the PTFPT film can be conveniently calculated by a simple expression:²⁰

$$\tau_{\rm d}(E) = \left[C_{\rm dif} / (\pi^{1/2} I t^{1/2} / \Delta E) \right]^2, \tag{2}$$

where $\tau_d(E)$ is the characteristic diffusion time constant of a specific part of the film from which the chemical diffusion coefficient D_i (related to this specific part) can be calculated: $D_i(E) = l^2/\tau_d(E)$. It is assumed that the characteristic diffusion length *l* is the film's thickness. Note that this assumption affects the absolute value of D_i rather than the plot of log D_i vs. potential, since the characteristic diffusion length is most probably invariant with the potential. The calculated value, $\tau_d = 12.3$ s, is marked in Fig. 4a.

Instead of determining the Cottrell parameter as minimum in Fig. 4a, one can use the conventional *I vs.* $t^{1/2}$ plot (see Fig. 4b). A straight line tangential to the short-time domain of the experimental curve, crossing the origin of the coordinates, results in exactly the same value of τ_d as that obtained from Fig. 4a. Involvement of slow kinetics and the secondary Cottrell domain are indicated in Fig. 4b, and can be compared with those marked in Fig. 4a.

It was interesting to examine the long-time domain of the response. This can be done using different current–time plots. In Fig. 4c we present the same experimental data in the form of a log|*I*| *vs. t* curve, appropriate for the identification of an exponential decay of the diffusion current with time, in the finite-space (long-time) domain.^{17,18,20,23} The diffusion time constants τ_d can be found from the linear portions of this plot, whose slope is $-\pi^2/4\tau_d$. From Fig. 4c it is seen that in the range of 50 < t/s < 125 the plot is linear, and the related τ_d is 120 s. However, in the range of 10 < t/s < 13, the effective value of τ_d is considerably smaller, about 53 s. Fig. 4c actually provides evidence that in the range of 10 < t/s < 50, the slope of the log *I vs. t* curve gradually decreases, and thus the effective values of τ_d increase accordingly.

In order to complete the comparison of the shape of the current transients for uniform and non-uniform films, we used the plot of the differential quantity, dlog|I(t)|/dlog t vs. dimensionless time, t/τ_d proposed by Montella.²³ The solid line in Fig. 4d relates to the case of semi-infinite (Cottrell) diffusion in the short-time domain, and to finite-space diffusion in the longtime domain (uniform electrode). The current was calculated with the use of the exponent series sum,²¹ which was previously used by us for modeling Li-ion diffusion in composite graphite electrodes,²⁴ and by Montella in his detailed analysis of the effect of charge-transfer kinetics and Ohmic potential drops on the determination of τ_d .²³ As seen from the solid line in Fig. 4d, the transition from the Cottrell domain to the finitespace diffusion domain occurs within a narrow time range near $t/\tau_{\rm d} = 0.2^{23}$ In the short-time domain, $(d\log |I(t)|/d\log t)$ is equal to -0.5 (Cottrell domain), whereas in the long-time domain, $(dlog|I(t)|/dlog t) = -(\pi^2 t/4\tau_d)^{.23}$ An interesting property of the plot dlog I(t) dlog t vs. t/τ_d for the case of a uniform electrode is that it does not depend on τ_d . In view of the considerable Ohmic potential drops and the kinetic contributions to the current transient of the PTFPT film under consideration, the horizontal plateau corresponding to (dlog|I(t)|/dlogt = -0.5 at $(t/\tau_d) < 0.2$, is absent in the experimental curve in Fig. 4d. In addition, in the range of $(t/\tau_d) > 0.2$, the experimental curve does not approach to the limiting straight line, and clearly demonstrates a concave shape. Comparison between Figs. 4d and c shows that the concave curve in the former figure corresponds to a gradual increase in the local value of τ_d . Thus, such an analysis of the shape of the dlog|I(t)|/dlog t vs. t/τ_d plot appears to be very useful in identifying the non-uniform character of doping of the PTFPT film under consideration.

It was significant to study how the non-uniform character of doping of the PTFPT film is reflected by parallel EIS measurements. Fig. 5a shows typical Nyquist plots for the PTFPT film during its n-doping at five selected potentials in the SF solution. In the high-frequency domain, a non-closed semicircle (HFS) appears as a result of the relatively high bulk polymer film resistance in the SF-based solution (see insert in Fig. 5a). This semicircle was absent in the impedance spectra of the same electrodes in the AN- and the PC-based solutions. Thus, the above high bulk film resistance deduced from the Nyquist plots for the PTFPT film in the SF solution could be the major reason for deviation of the current transients described above, from the Cottrell behavior in the short-time domain (see Fig. 4). This high, potential-dependent bulk film resistance probably arises because of insufficient swelling of the film in the SF solution. Thus, a correlation between the related PITT, CV, and EIS characteristics of the PTFPT film in the SF solution has been obtained.

Our major focus is on the portions of the Nyquist plots related to the medium-to-low frequency domain, because they reflect the impact of diffusion. The insert in Fig. 5a shows that a potential-dependent, medium-frequency semicircle (MFS) appears on the right-hand side of the HFS. Fitting the MFS using a simple equivalent circuit analog shows that the capacitance in its maximum is of the order of 6 μ F cm⁻², *i.e.*, close to a typical double-layer capacitance. Taking into account the fact that the coupled resistance decreases as the doping level of the film increases, the MFS was ascribed to slow, interfacial ion-transfer kinetics. At the beginning of the n-doping (E =1.6 V vs. Li/Li⁺), as is seen from Fig. 5a, an extensive, depressed, HFS overlaps with the MFS. This latter semicircle, in turn, overlaps with the very narrow (in terms of the frequency range) Warburg-type response, which approaches a limiting, distributed capacitance behavior (constant-phase element, CPE) in the limit of the very low frequencies.

Fig. 5b presents a detailed Nyquist plot measured with the PTFPT film during its n-doping at 1.6 V (*vs.* a Li ref. electrode). This plot is used as an example for the analysis of τ_d obtained by EIS in the high- and the low-frequency domains, and for a comparison of the τ_d values obtained by EIS and PITT.

Similar to the short-time domain of the PITT response eqn. (2), the high-frequency Warburg-type EIS response can be conveniently treated in terms of the differential capacitance, $C_{\text{dif}} = Q_{\text{m}} d\theta / dE$ (equilibrium characteristic), and the Warburg slope, A_{w} (a kinetic characteristic), where $A_{\text{w}} = \Delta \text{Re}/\Delta \omega^{-1/2} = \Delta \text{Im}/\Delta \omega^{-1/2}$ (ΔRe and ΔIm are the differences in the real and the imaginary components of the impedance, respectively, corresponding to a finite variation in the angular



Fig. 5 Nyquist plots measured with an n-doped PTFPT film in contact with a SF-based electrolyte solution at five different potentials as indicated (a) and the detailed Nyquist plot for the slightly doped film (b). The Warburg and the low-frequency, distributed capacitance lines are marked. Insert in Fig. 5a is an enlarged view of the high-frequency domain of the plots shown in (a). For other details see the text.

frequency of the ac current, $\Delta \omega$). The diffusion time constant, τ_d , is then simply a product of both the above quantities²⁰ (compare with similar equation in ref. 25):

$$\tau_{\rm d} = 2[Q_{\rm m}A_{\rm w}{\rm d}\theta/{\rm d}E]^2, \qquad (3)$$

where $\tau_d = l^2/D_i$; Q_m is the maximal doping (undoping) charge and θ is the dimensionless doping level.

For ideally uniform films, the values of τ_d obtained by PITT in the short-time domain should coincide with those obtained by EIS in the high frequency, Warburg region. This can be easily proved: by equating the τ_d from eqns. (2) and (3) one obtains the intrinsic relation between the characteristic kinetic parameters of the PITT and EIS responses, *i.e.*, between $It^{1/2}/\Delta E$ (ΔE is the amplitude of the potential step) and A_w :

$$A_{\rm w} = (2\pi)^{-1/2} \Delta E / I t^{1/2}.$$
 (4)

It is seen from eqn. (4) that the product of these parameters is equal to $(2\pi)^{-1/2}$, *i.e.*, to a universal constant connecting together the direct and the alternative current responses.

Determination of τ_d for the PTFPT film polarized at 1.6 V using eqn. (3) results in $\tau_d^{\text{high}\omega} = 11.4 \text{ s}$, *i.e.*, 3.5 times less than that found from PITT ($\tau_d^{\text{PITT}} = 40 \text{ s}$). Both these values are indicated in Fig. 5b. Thus, we observed a pronounced

difference between the values of τ_d obtained by the two techniques in the same time domain that we have never seen before during our study of a variety of lithiated inorganic host mate-rials.^{20,26-28} Note, however, that the Ohmic potential drops and the kinetic limitations for these latter materials in contact with typical for Li-ion battery aprotic electrolyte solutions were never so great as that for the PTFPT film, in contact with SF solutions. We suggest that the large bulk film resistance in the SF solution, as is seen from the insert in Fig. 5a, leads to the fact that the $It_{Cottrell}^{1/2}$, calculated is lower than the true value because of the interference of the high resistance, which does not allow $It_{\text{Cottrell}}^{1/2}$ to be measured precisely, from which τ_{d} is calculated. Thus, the minimum in $It^{1/2}$ vs. log t, as seen in Fig. 4a, can be considered only as a rough estimate of $It_{Cottrell}^{1/2}$. The use of EIS for the determination of τ_d should be more advantageous, as this allows more effective separation of the medium-frequency Warburg response from the Ohmic and the bulk film impedance (see Fig. 5a). However, as is seen in the same figure, separation between the Warburg domain and the medium-frequency kinetic semicircle, especially at low doping levels, is not very good (in the case of lithiated inorganic hosts usually much better separation could be obtained²⁰). The above intrinsic difference between the two techniques, as refers to their ability to discriminate between the contributing high- and medium-frequency processes, should always be kept in mind. Note also that the worst technique in this respect is CV, since such high-frequency characteristics as the Ohmic potential drops in the solution and in the film's bulk directly affect the shape of the low-frequency response, *i.e.*, the shape of the CV curves.

It was interesting to evaluate τ_d from the low-frequency domain of the impedance spectra. The case of a finite-space diffusion (low-frequency response) for uniform electrodes could be conventionally treated in terms of a product of the limiting, low-frequency capacitance C_L (coinciding with the earlier introduced C_{dif}), and the related low-frequency resistance:²⁵

$$\tau = 3R_{\rm L}C_{\rm L}.\tag{5}$$

The main problem related to the practical application of eqn. (5), is the determination of R_L and C_L from the experimental Nyquist plot, which shows a great deal of non-ideality (see Fig. 5b): the low-frequency domain of these Nyquist plots can be approximated by a constant-phase-element, CPE. We estimated R_L from the Nyquist plot as was proposed by Pickup *et al.*,^{29–31} *i.e.*, from the intercept between the Warburg line and the sloping capacitive line (the CPE-like line), see Fig. 5b.

Calculation of τ_d from the low-frequency domain using eqn. (5), and the value for the low-frequency resistance $R_{\rm L}$, as indicated in Fig. 5b, and C_L , taken from the parallel PITT measurements, results in $\tau_d^{low\omega} = 4.1$ s. Thus, the diffusion time constant obtained from the low-frequency range, appears to be almost three times smaller than that estimated from the Warburg domain ($\tau_d^{high\omega} = 11.4$ s), and about an order of magnitude smaller than that obtained from PITT, $\tau_d^{\text{PITT}} = 40$ s). The most probable reason for the reduced value of $\tau_d^{low\omega}$ is an underestimation of $R_{\rm L}$ obtained from the transitional, CPE-like low-frequency line. In fact, the extrapolation procedure depicted in Fig. 5b allows the determination of $\tau_d^{\hat{l}ow\omega}$ from a limited, low-frequency domain of the film's impedance spectra. However, due to the film's non-uniformity, this transitional domain corresponds to a continuous distribution of τ_d , as we saw from the analysis of the PITT response (Fig. 4c). Direct impedance modeling of such non-uniform film's response shows that extrapolation from a limited, transitional domain to high frequencies may lead to severe underestimation of R_{L}^{21} (see also Fig. 4 in ref. 22 and Fig. 5 in ref. 32). Careful analysis of the slope of these transitional impedance domains shows that only slight deviations

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of the film's behavior from that typical for uniform films, can justify the method of estimation of $R_{\rm L}$ according to Pickup *et al.*^{29–31}

Thus, both analyses of the current transients (PITT) and the Nyquist plots (EIS) related to the PTFPT electrodes in SF solutions indicate that doping the PTFPT film is essentially non-uniform. This, of course, considerably complicates the analysis of the potential dependences of τ_d or the related D_i . In the case of uniformly doped CP films, with a single τ_d for the whole film electrode, the shape of the plot D_i vs. *E* allows the identification of the nature of the interaction between the electronic and ionic species at their sites inside the film.^{20,26,33} When D_i is independent of *E*, such interactions are absent, and the doping can be expressed by a Langmuirian (Nernstian) isotherm.^{20,33} The curve with a maximum usually suggests repulsive interactions.^{20,26,33}

It is clear that the analysis of the potential dependences of D_i for the non-uniform electrodes becomes very complicated. Because of a considerable underestimation of $R_{\rm L}$, and thus $\tau_{\rm d}$ and $D_{\rm i}$, when treating low-frequency impedance spectra, we must exclude the related results from the discussion because they are not sufficiently reliable. Thus, only the potential dependences of D_i obtained from PITT and high-frequency impedance spectra should be compared. The chemical diffusion coefficients of the inserted ions, calculated from the related τ_d , are shown in Figs. 6a and b as a function of potential for the p- and n-doping, respectively. As discussed above, the τ_d values calculated from PITT measurements of the PTFPT electrodes in SF are not accurate. However, they reflect a clear trend of the diffusion time constants, as a function of potential. It can be seen that the plots, both for the doping and the undoping, are peak-shaped, as is expected for repulsive interactions between the inserted species. We assume that the shape of the D_i vs. E plots obtained from PITT for the non-uniform electrode is also as meaningful as that calculated for uniform electrodes, for certain, particular types of non-uniformity. This can be proved by direct comparison of D_i obtained from the PITT and the high-frequency impedance measurements. As seen in Fig. 6b, the shape of D_i vs. E curves, both for n-doping



Fig. 6 Potential dependencies of the chemical diffusion coefficient, $\log D_i$, for the p-doping/undoping (a) and the n-doping/undoping (b). For the latter case, the values of D_i were obtained from both PITT and the high-frequency impedance spectrum of the film.

and undoping, is roughly the same, except for the slightly undoped film. The absolute values of D_i obtained from the impedance data are approximately 4 times larger than that which followed from PITT. The reason for this difference has been discussed above. We can imagine two different cases of the film's non-uniformity. The first considers the film as a variety of fibrils having a different, but potential-independent, size. The extent of film swelling may be potential dependent but identical for the fibrils of different size. In this case, D_i will be independent of the individual fibril sizes but there will be a distribution of different τ_d in the time domain of the related measurement technique (i.e. PITT and EIS). If this is the case, the D_i in Fig. 6 could be interpreted as effective values of D_i obtained for a specific (short) time domain using conventional finite-space models for uniform electrodes. Since for this particular case of the film's non-uniformity the individual values of $D_{\rm i}$ at constant potential do not depend on the size of the fibrils, potential dependences of effective D_i obtained in the highfrequency domain (i.e. of the Warburg-type) may reflect true potential dependences of the individual D_i . In order to either confirm or refute this type of non-uniformity, reliable models for quantitative treatments of non-uniformity are required. Alternatively, if the fibrils have essentially the same size, but have a different chemical environment (i.e., differently impregnated with the solvent), a distribution of different D_i will certainly result in the related distribution of τ_d . We cannot distinguish this type of film non-uniformity from the former one on the basis of electrochemical methods only. This is because these methods actually provide the determination of $\tau_{\rm d}$, whereas $D_{\rm i}$ is calculated from the simple expression for linear diffusion $D_i = l^2 / \tau_d$. Direct *in situ* observations of CP films' morphology at different doping levels may be desirable for understanding the essential features of non-uniformity of doped CP films.

Conclusion

The electroanalytical characterization of PTFPT electrodes in SF-based solutions using CV, PITT, and EIS, shows a great deal of similarity in the mechanism of the film's p- and ndoping. This relates to the maximum stored charge and the potential dependence of the differential capacity, C_{dif} , and the chemical diffusion coefficient of the inserted ions, D_i . We analyzed the shape of the time-dependent current responses during PITT characterizations. A major, short-time Cottrell domain in the current transients was seen in all the individual potential steps. In order to study the PTFPT film's non-uniformity during doping, we carefully analyzed experimental current responses during potentiostatic titrations using $d\log |I(t)|/d\log t$ vs. t/τ_d plots. A drastic diminution of the length of the Cottrell domain in this plot has two different sources. In the short-time limit, this diminution, as well as a decrease in the Cottrell parameter, $H_{\text{Cottrell}}^{1/2}$ (compared to the true one), reflects a strong effect of the Ohmic potential drop across the film's bulk measured (when doped in the SF solution) in the semi-infinite, diffusion domain. Very large bulk film resistance, directly observed by EIS, is one of the most characteristic features of PTFPT electrodes doped in SF solutions. Unfortunately, this was not the only complication related to quantitative description of the shape of the current transients during PITT. At longer times, this transient tends to show a continuous distribution of τ_d rather than the expected, logarithmic decay of the current with time, characterized by the same τ_d as that in the short-time domain. This behavior is clear evidence of a non-uniform film doping. The conclusion on the non-uniform PTFPT film doping in the SF solution is in line with the sluggish kinetics of the film's swelling in this solution studied by CV. Further experimental studies on the effect of non-uniform doping of CP films, should

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