

A COMPARATIVE STUDY ON THIN POLY-N-METHYLPYRROLE AND POLYPYRROLE FILMS

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Growth, cycling, and overoxidation of thin poly-N-methylpyrrole (PMePy) films was studied in 0.5M LiClO₄-propylene carbonate electrolyte. N-methylpyrrole starts to polymerize at about 3.53 V vs Li/Li⁺. The redox potential of PMePy is about 0.6 V more positive than that of polypyrrole (PPy). The overoxidation thresholds of both PMePy and PPy are, however, almost identical (3.8–3.9 V vs Li/Li⁺). Low doping levels, of the order of $y \approx 25\%$, are therefore reached during the nearly reversible potentiodynamic cycling of PMePy in the 2.0–4.0 V range, in contrast to $y \approx 42\%$ attainable on polypyrrole (PPy) under the same conditions. Continuous slight decrease of the coulombic capacity of the polymer with the cycle number, attributed to an irreversible overoxidation, is observed. Addition of 1 vol. % of water into the growth electrolyte does not improve the doping level of the PMePy film. Due to the poor electrochemical performance of thin PMePy films with respect to battery application, higher energy densities as offered from the Li/PPy system are not to be expected.

The formation of a polymer by oxidation of pyrrole units is known from the beginning of this century¹. Layers of polypyrrole (PPy), poly-N-methylpyrrole (PMePy), and also of other similar polymers, are electronically conducting, and show interesting electrical, electrochemical, and optical properties^{2–4}. Many applications were suggested, ranging from batteries through modified electrodes and optical devices to the protection of photoanodes against corrosion.

Polypyrrole received much interest⁴. On the other hand, only few reports appeared, in which also basic properties of PMePy were mentioned^{5–10}. Poly-N-methylpyrrole possesses an about 600 mV higher oxidation potential than polypyrrole⁷. This could result, despite the higher molecular weight, in a slightly higher energy density of the system Li/PMePy as compared to a Li/PPy battery. This is the main argument why PMePy and composite PPy–PMePy films are considered as possible candidates for positive active materials of lithium batteries^{4,5}.

In order to get a reliable basis for the selection of polymers promising for scale-up experiments we compared growth, cycling and overoxidation of PMePy and PPy

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films in propylene carbonate-based electrolytes, i.e. under conditions compatible with the present lithium battery technology. Applied battery testing is usually performed under galvanostatic conditions. The absence of well-defined plateaus makes, unfortunately, the evaluation of galvanostatic curves less straightforward than the assignment of peak-shifts in cyclic voltammograms imposed by both polymer cycling and partial overoxidation. For the comparative studies we therefore selected potentiodynamic cycling.

The initial current efficiency for the electropolymerization of pyrrole is not constant^{2,4}. Thus, one has to be very cautious to determine coulombic capacities (doping levels) from the results on thin layers. However, measurements on very thin layers can be used to determine preliminary, approximate values of doping levels in a short time. Results on thin layers may then be the basis for the decision whether the complementary scale-up experiments should be performed.

EXPERIMENTAL

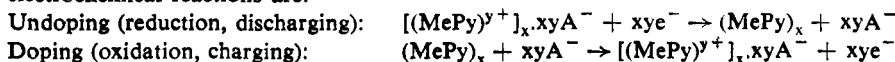
All manipulations during the preparation of electrolytes and the construction of cells were performed either under vacuum or in a dry Ar-filled glove box (< 50 ppm H₂O). Propylene carbonate (PC, Burdick & Jackson, "distilled in glass") was dried by boiling under vacuum for 3 h prior to the electrolyte preparation. LiClO₄ (Fluka p.a.) was dried at about 150°C under vacuum overnight. Both N-methylpyrrole (MePy, Merck) and pyrrole (Py, Riedel-de Haën) were vacuum-distilled prior the use in order to remove coloured species present in as-received chemicals. The base electrolyte used, 0.5M LiClO₄ in PC, was dried several weeks over lithiated 4Å molecular sieves to reach less than 20 ppm of water content ("dry" electrolyte), as measured by the Karl-Fischer titration.

In order to exclude oxygen influence, both the polymer synthesis and cycling were performed inside the Ar-filled glove box in sealed glass cells. Excess-electrolyte-containing, four-compartment cells with the central working electrode surrounded by two large lithium-strip counter electrodes and a Li reference electrode (against which all potentials in this paper are referred) were used. Each of the Li electrodes was separated from the working electrode compartment by a 1 mm thick glass frit. Measurements were performed at room temperature.

Poly-N-methylpyrrole was deposited on Pt- or Au-sheet current collectors (2.0 cm² both sides) from either "dry" (< 20 ppm H₂O) or "wet" (with 1 vol. % H₂O added) 0.2M MePy + 0.5M LiClO₄/PC electrolytes. Immediately after the synthesis, the working electrode was always removed from the cell, washed in the dry 0.5M LiClO₄/PC solution, and then placed in the other cell filled also with the dry 0.5M LiClO₄/PC electrolyte. It was undoped* by sweeping the electrode potential from its open circuit value (OCV) to 2.0 V at 1 mV/s. Subsequently, the potential was held for 60 min at 2.0 V to ensure the total reduction.

After the first undoping, the polymer electrodes were potentiodynamically cycled at 1 or 10 mV/s. The anodic (Q_{Charge}) and cathodic ($Q_{\text{Discharge}}$) charge (coulombic capacity) was on-line integrated and stored in a microcomputer.

* The as-grown polymer (MePy)_x is doped with perchlorate anions (A⁻). Its reversible electrochemical reactions are:



RESULTS AND DISCUSSION

N-Methylpyrrole Electropolymerization

Electropolymerization of pyrrole (Py) from the 0.2M Py + 0.5M LiClO₄/PC electrolyte starts at about +3.47 V. Both dry and wet electrolytes gave nearly the same current-potential dependence¹¹ in the 3.46–3.70 V interval. The comparison between the stationary and potentiodynamic current densities showed that at the very slow sweep rates of about 0.1 mV/s a nearly steady-state polymerization current is reached¹¹. Therefore, the sweep rate of 0.1 mV/s was used in this study.

As can be seen from Fig. 1, the polymerization of N-methylpyrrole from the dry 0.2M MePy + 0.5M LiClO₄/PC electrolyte at Pt substrates starts nearly at the same potential as in the pyrrole case. The current-potential curves are, however, not identical. The deviation from the background current at the very beginning of the MePy polymerization is less pronounced. At about +3.53 V the polymerization current increases significantly. The reproducibility of this value is very good; the potential readings at the same current densities were 3.53, 3.54, and 3.53 V for three independent runs.

Following conclusions were drawn from our experiments:

1. No recognizable difference was found between the current-potential curves taken on Pt and Au substrates.
2. Addition of 1 vol. % of water into the electrolyte shifted the recognizable beginning of the polymerization from 3.53 V to about 3.57 V (Fig. 1).

There is another conspicuous difference between the polymerization from the dry and wet electrolytes. After passing the same charge (240 mC/cm²) at 3.70–3.75 V, the electrolyte in the positive-electrode compartment was dark in the dry case (gold-brown, "tea" colour). The wet electrolyte was, however, nearly colourless. Thus, in the wet case significantly less coloured soluble species is produced during the electropolymerization.

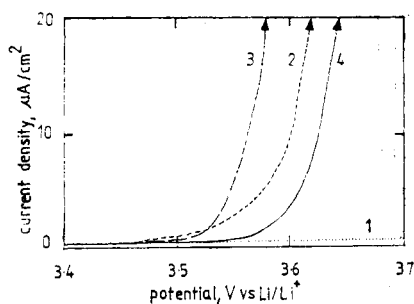


FIG. 1

Voltammetric curves at 0.1 mV/s for a Pt electrode in 0.5M LiClO₄/PC electrolyte. 1 Base, dry electrolyte; 2 dry electrolyte with 0.2M pyrrole; 3 dry electrolyte with 0.2M N-methylpyrrole; 4 wet electrolyte with 1 vol. % H₂O + 0.2M N-methylpyrrole

For each of the above described runs, fresh electrolyte was used. If the brown dry solution generated during the polymerization remained in the cell and a voltammetric run with a clean Pt substrate was started, the polymerization current deviated significantly from the background at about 3.50 V instead of at 3.53 V. Thus, the presence of coloured species, generated during previous experiments, only slightly influences the polymerization potential.

To reach good electrochemical performance of polypyrrole films, galvanostatic synthesis at rather low current density, $250 \mu\text{A}/\text{cm}^2$, was recommended¹¹⁻¹³. Consequently, the electrode potential remains below 3.9 V (the beginning of a strong, irreversible PPy oxidation¹² in LiClO_4/PC) during the polymer growth in both dry and wet electrolytes.

Attempts to polymerize N-methylpyrrole from the 0.2M MePy + 0.5M LiClO_4/PC electrolyte galvanostatically at $250 \mu\text{A}/\text{cm}^2$ showed, in contrast to the PPy case, obvious differences when the polymer was grown under dry and wet conditions, respectively. During the dry synthesis, a rather stable potential of about 3.7 V was recorded. In the wet case, however, the electrode potential reached about 4.1 V rapidly and increased with time significantly further.

It is known that the introduction of N-substituents as a rule results in a decrease in electronic conductivity of the doped polypyrroles^{7,9}. Furthermore, irreversible oxidation (overoxidation) of polypyrrole films lowers the conductivity to that of insulating materials¹⁴. We assume, therefore, that an ohmic drop across the PMePy layer and/or a formation of an overoxidized polymer were responsible for the observed increased electrode potential under wet conditions. The difference in the polymerization potential recorded during the galvanostatic runs could thus mean that the electronic conductivity of very thin PMePy layers formed under wet conditions is initially lower than that of the dry polymers. The increased electrode potential causes then faster overoxidation followed by a further increase of the IR drop across the layer.

In order to obviate a possible degradation of electrochemical properties of the polymer caused by its partial irreversible overoxidation during the synthesis¹², PPy and PMePy films grown potentiostatically at low potentials (3.70–3.75 V) were used for further studies. Polypyrrole grown at low current density, and, consequently, at low potential is known to yield compact films¹³. To avoid possible influence of the ohmic drop and solid-state diffusion during both the polymer growth and fast cycling, $50 \text{ mC}/\text{cm}^2$ were allowed to pass during the polymerization. This charge forms about $0.1 \mu\text{m}$ thick poly-N-methylpyrrole layers⁷.

First Undoping

The importance of the very slow, complete undoping of the as-grown polypyrrole layers was recognized by different research groups^{11,12,15-20}. The $1 \text{ mV}/\text{s}$ potenti-

dynamic first-discharge curves allow to estimate the PPy type¹². The dry polypyrroles show several broad, overlapping reduction peaks in the 3.4–2.2 V potential interval, the wet ones only a very sharp, single peak at about^{11,12} 2.6 V.

In Fig. 2, the first potentiodynamic discharges of dry and wet poly-N-methylpyrroles are compared. In contrary to the PPy case, both dry and wet PMePy films show a rather similar first-discharge behaviour. Furthermore, the shape and potentials (Table I) of reduction peaks recorded on PMePy films during their subsequent cycling approached the curves and values measured during the first undoping. Experiments with the very thin PPy layers, grown also on Pt at 3.70 V and 50 mC/cm², confirmed the same PPy characteristics as found previously on 1–50 μm thick layers^{11,12,21} and revealed thus that the observed difference between the first-discharge behaviour of PPy and PMePy films is not due to the measurements performed on very thin polymer layers.

Thus, the as-grown, "virgin" poly-N-methylpyrrole probably does not undergo such a phase transition ("polymer relaxation", changing redox properties of the material) during the first discharge as found for the "virgin" PPy^{11,12,19}. Therefore, it seems reasonable to suggest that already during the synthesis of poly-N-methylpyrrole a structure is formed, which could be similar to that of "relaxed" PPy, and which shows the same redox-properties as that of "cycled" PMePy polymer.

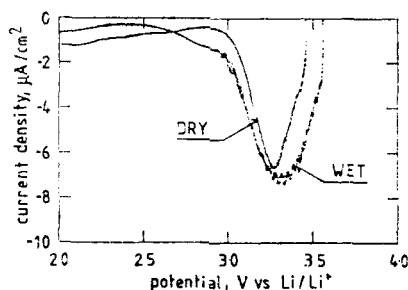
TABLE I

Reduction peak potentials (in V) of dry and wet poly-N-methylpyrroles

Synthesis	First discharge at 1 mV/s	Cycling at 10 mV/s	
		1st cycle	1 000th cycle
dry	3.26	3.34	3.43
wet	3.31	3.32	3.44

FIG. 2

First potentiodynamic discharge at 1 mV/s of poly-N-methylpyrrole layers, synthesized at 3.70 V (vs Li/Li⁺) and 50 mC/cm² on a Pt substrate in dry 0.2M MePy + 0.5M LiClO₄/PC, and wet (with 1 vol. % H₂O added) electrolytes



Cycling of Poly-N-methylpyrrole

Both polypyrrole^{11,12} and poly-N-methylpyrrole electrodes need about 10 cycles to develop a nearly stable cyclic voltammograms. During subsequent cycling, a slight decrease of the coulombic capacity with the cycle number is observed. In Fig. 3, the 50th cycles recorded on dry and wet PMePy samples are compared. Both curves show a shape typical for conducting polymers¹⁹ — a peak pair followed at higher potentials by a pseudocapacitive part of the cyclic voltammogram. As expected⁷, the peaks lie at about 3.4 V, i.e. about 0.6 V more positive than found for PPy electrodes¹¹.

Fig. 3 shows that the wet PMePy form possesses less coulombic capacity when cycled. This could be an indication that the doping level attainable with the wet polymer is lower than that of the dry one. Another consistent explanation could be, however, deduced from the fact that the exact amount of the polymer grown at 50 mC/cm² is unknown. If water present in the electrolyte decreases the efficiency of the polymer growth (e.g. by promoting the formation of dimers or other similar soluble, colourless species), the amount of the polymer at the substrate could differ although the PMePy layers were synthesized by passing the same charge.

The different current densities reached during the synthesis at 3.70 V, about 200 $\mu\text{A}/\text{cm}^2$ in the dry electrolyte in contrast to only about 5 $\mu\text{A}/\text{cm}^2$ in the wet one, show the significant differences in the total time necessary for the polymer growth. Thus, more charge could be consumed by side reactions in the wet case.

In Fig. 4, the development of cyclic voltammograms of wet PMePy films with the cycle number is shown. Cycling properties similar to that found earlier for "poor"

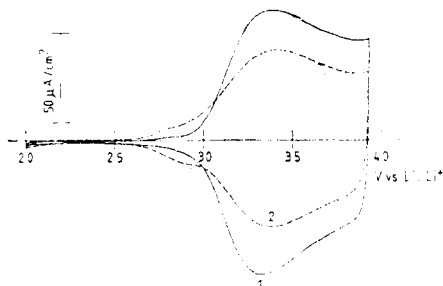


FIG. 3

Cyclic voltammograms of 50 mC/cm² PMePy layers, synthesized on Pt under dry and wet conditions. Sweep rate 10 mV/s, potential window 2.0 to 3.9 V (vs Li/Li⁺), 50th cycle; electrolyte dry 0.5M LiClO₄/PC; 1 dry synthesis at 3.70 V; 2 wet synthesis at 3.75 V

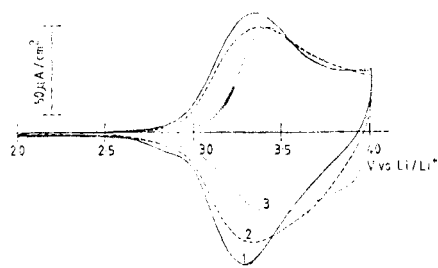


FIG. 4

Cyclic voltammograms of a PMePy layer, synthesized at 3.70 V and 50 mC/cm² on Pt under wet conditions. Sweep rate 10 mV/s, potential window 2.0 to 4.0 V (vs Li/Li⁺); electrolyte dry 0.5M LiClO₄/PC; 1 1st cycle; 2 50th cycle; 3 1000th cycle

polypyrrole films¹¹ were registered — a slight decrease of the coulombic capacity with the cycle number accompanied by the shift of both, oxidation and reduction peaks toward more positive values. The anodic pseudocapacitive parts of the voltammogram did not significantly change with the cycle number. We explain such behaviour by a gradual slight loss of the most negative redox-sites in the polymer, probably due to their irreversible overoxidation during cycling.

Similar peak shift is also seen on the curves taken on the dry PMePy samples (Fig. 5). However, in contrast to the results shown on the wet polymer (Fig. 4), the anodic pseudocapacitive region of the voltammogram in Fig. 5 changes significantly with the cycle number. This indicates a much higher sensitivity of the as-grown dry poly-N-methylpyrrole form toward its degradation (overoxidation) during cycling.

All cycling results are summarized in Fig. 6, where the cathodic charge from cyclic voltammograms, i.e. the coulombic capacity of the polymer, is recorded as a function of the cycle number. The coulombic capacity of the dry PMePy form drops with the cycle number significantly faster than found on the wet polymer. This, and also the strong changes on the dry curve imposed by the slight increase in the upper potential limit of cycling from 3.9 to 4.0 V, support the assumption that the dry poly-N-methylpyrrole degradation is rather fast during cycling.

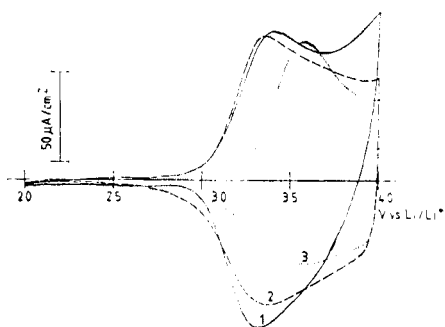


FIG. 5

Cyclic voltammograms of a PMePy layer, synthesized at 3.70 V and 50 mC/cm² on Pt under dry conditions. Sweep rate 10 mV/s, potential window 2.0 to 4.0 V (vs Li/Li⁺); electrolyte dry 0.5M LiClO₄/PC. 1 1st cycle; 2 50th cycle; 3 1 000th cycle

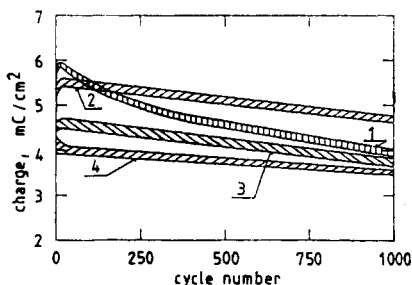


FIG. 6

Cathodic charge from cyclic voltammetry at 10 mV/s of PMePy layers synthesized at 3.70 V and 50 mC/cm² on Pt under dry and wet conditions as function of cycle number. Electrolyte 0.5M LiClO₄/PC: 1 dry, cycled between 2.0 and 4.0 V; 2 dry, cycled between 2.0 and 3.9 V; 3 wet, cycled between 2.0 and 4.0 V; 4 wet, cycled between 2.0 and 3.9 V

The irreversible degradation (overoxidation) also affects the current efficiency values, $Q_{\text{Disch}}/Q_{\text{Charge}}$ recorded during the polymer cycling. All samples needed about 50 cycles at 10 mV/s to reach a steady state value. The ratio $Q_{\text{D}}/Q_{\text{C}}$ was then close to 1.000 for all wet samples, i.e. no difference between the anodic and cathodic charges was found within the accuracy of our equipment (~ 0.003). The same result was also measured for dry samples cycled in the 2.0–3.9 V potential window. In the 2.0–4.0 V range, a slight difference between the anodic and cathodic charge was detected for the dry PMePy electrodes ($Q_{\text{D}}/Q_{\text{C}} \approx 0.995$).

The approximate doping levels estimated from the nearly stable Q_{D} values measured over 1 000 cycles on both PMePy forms are significantly lower than the value of $y \geq 0.42$ estimated earlier for thicker polypyrrole foils¹². Coulombic capacity of the best thin poly-N-methylpyrrole layers (Fig. 6) corresponds to about one electron per four pyrrole rings ($y \approx 0.25$) only. As discussed above, electrochemical estimation of y values is a very rough approximation. However, with respect to the differences in the doping levels attainable on thin layers and to the monomer unit weight, we do not recommend poly-N-methylpyrrole for scale-up battery experiments.

Overoxidation of Poly-N-methylpyrrole

In order to understand better the irreversible overoxidation we performed the following experiment on some samples: After 1 000 cycles at 10 mV/s in the 2.0–4.0 V interval were reached and the PMePy electrochemical performance was rather stable, the sweep rate of 1 mV/s was applied and several "reversible" cycles were recorded in the same potential window. Then the potential interval was extended to 5.5 V which caused almost complete irreversible overoxidation of the polymer. Very low electrochemical activity of the electrode was detected after such overoxidation run.

Overoxidation behaviour of dry and wet poly-N-methylpyrrole is compared in Fig. 7. In the dry case the anodic current begins to increase at about 3.8 V, in the wet one at about 3.9 V, an indication that the very beginning of the overoxidation process lies already below 4 V in both cases. The overoxidation threshold of cycled poly-N-methylpyrrole (3.8–3.9 V) is thus approximately the same as found¹² for cycled polypyrrole (3.9 V) in the identical electrolyte, dry 0.5M LiClO₄/PC. The maximum levels of reversible doping obtainable on PPy and PMePy electrodes are thus limited in both cases by the same potential limit.

As follows from Figs 6 and 7, the wet PMePy is slightly less sensitive against irreversible degradation (overoxidation) than the dry polymer, again in accordance with the findings on wet and dry polypyrroles^{11,12}.

The charges consumed by the total overoxidation of PPy and PMePy are also similar – roughly 1 e^- per pyrrole ring was estimated during our runs. Thus, the

overoxidation of poly-N-methylpyrrole in dry LiClO_4/PC seems to proceed via a similar reaction mechanism as in the polypyrrole case. This implies that the nitrogen atom with its substituent is not affected by the overoxidation reaction.

CONCLUSIONS

1. N-methylpyrrole starts to polymerize from the dry $0.2\text{M MePy} + 0.5\text{M LiClO}_4/\text{PC}$ electrolyte at about $+3.53\text{ V vs Li/Li}^+$. Addition of 1 vol. % of water to this electrolyte shifts the observable beginning of the polymerization to about $+3.57\text{ V}$.

2. Opposite to the findings on polypyrrole, the potential and the shape of the reduction peak are similar during the first discharge of the as-grown poly-N-methylpyrrole and during its further cycling.

3. The degradation (overoxidation) of cycled poly-N-methylpyrrole starts at about $3.8\text{--}3.9\text{ V vs Li/Li}^+$, which strongly limits the potential window suitable for the reversible cycling. Polymer grown from the wet electrolyte is slightly less sensitive against overoxidation, its coulombic capacity is, however, lower than that of the polymer synthesized from the dry electrolyte.

4. Considerably higher redox potential of poly-N-methylpyrrole (about 3.4 V for PMePy, against about 2.8 V for PPy) cannot increase the total energy density of the polymer electrode when PMePy application in batteries is expected. The increased monomeric unit weight, many orders of magnitude lower conductivity of PMePy than that of PPy⁷, lower doping level of PMePy ($y_{\text{max}} \approx 25\%$, in contrast to $y \geq 42\%$ found on PPy¹²), poor contact of thicker PMePy layers with the current

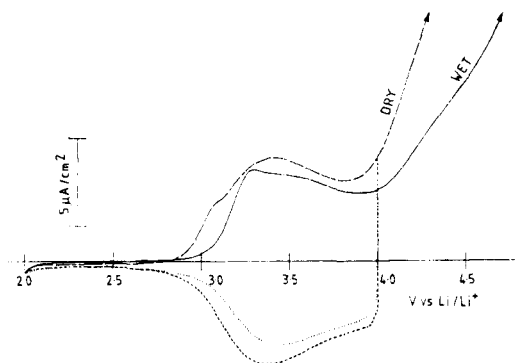


FIG. 7

1 mV/s voltammetric curves for the "reversible" cycling and overoxidation of dry and wet PMePy layers (synthesized at 3.70 V and 50 mC/cm^2 on a Pt substrate) in dry $0.5\text{M LiClO}_4/\text{PC}$ electrolyte. Curves were taken after 1000 cycles at 10 mV/s between 2.0 and 4.0 V

collector, and the identical overoxidation potential limits of PPy and PMePy, these all are disadvantages of poly-N-methylpyrrole as electrode active material.

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REFERENCES

1. Angeli A.: *Gazz. Chim. Ital.* **46**, 279 (1916).
2. Heinze J.: *Top. Curr. Chem.* **152**, 1 (1990).
3. Diaz A. F., Kanazawa K. K., Gardini G. P.: *J. Chem. Soc., Chem. Commun.* **1979**, 635.
4. Skotheim, T. A. (Ed.): *Handbook of Conducting Polymers*, Vol. I, II. Dekker, New York 1986 and references therein.
5. Naoi K., Hirabayashi T., Tsubota I., Osaka T.: *Bull. Chem. Soc. Jpn.* **60**, 1213 (1987).
6. Kanazawa K. K., Diaz A. F., Will W., Grant P., Street G. B., Gardini G. P., Kwak G.: *Synth. Met.* **1**, 329 (1980).
7. Diaz A. F., Castillo J. I., Logan J. A., Lee W.-Y.: *J. Electroanal. Chem.* **129**, 115 (1981).
8. Kanazawa K. K., Diaz A. F., Krounbi M. T., Street G. B.: *Synth. Met.* **4**, 119 (1981).
9. Diaz A. F., Bargon J. in: *Handbook of Conducting Polymers* (T. A. Skotheim, Ed.), Vol. I, p. 81. Dekker, New York 1986.
10. Yaniger S. I., Vidrine D. W.: *Appl. Spectrosc.* **40**, 174 (1986).
11. Novák P., Vielstich W.: *J. Electrochem. Soc.* **137**, 1036 (1990).
12. Novák P., Vielstich W.: *J. Electrochem. Soc.* **137**, 1681 (1990).
13. Bittihn R., Ely G., Woeffler F., Münstedt H., Naarmann H., Naegele D.: *Makromol. Chem., Macromol. Symp.* **8**, 51 (1987).
14. Elfenthal H., Schultze J. W., Thyssen A.: *Z. Phys. Chem., N. F.* **160**, 69 (1988).
15. Beck F.: *Electrochim. Acta* **33**, 839 (1988).
16. Beck F., Oberst M., Braun P.: *DECHEMA-Monographien* **109**, 457 (1987).
17. Beck F., Oberst M.: *Makromol. Chem., Macromol. Symp.* **8**, 97 (1987).
18. Heinze J., Dietrich M., Mortensen J.: *Makromol. Chem., Macromol. Symp.* **8**, 73 (1987).
19. Heinze J., Störzbach M., Mortensen J.: *Ber. Bunsenges. Phys. Chem.* **91**, 960 (1987).
20. Trinidad F., Alonso-Lopez J., Nebot M.: *J. Appl. Electrochem.* **17**, 215 (1987).
21. Novák P.: Unpublished results.