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## Reactions of solute species at an electrode modified with titanocene functionalized polypyrrole film: ferrocene and titanocene dichloride

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**Abstract** We have studied for the first time the ability of a conducting polymer film, p(Tc3Py), representing a polypyrrole matrix with covalently attached titanocene dichloride (TcCl<sub>2</sub>) centers, to serve as an intermedialtor for the electron charge transport between the electrode and the reaction sites of solute reactants. The standard potential of the first of these electroactive species, ferrocene (Fc), is in the range where the polymer matrix is in its slightly oxidized state so that solute Fc species give a reversible response at the surface of this modified electrode. Another solute reactant, TcCl<sub>2</sub>, was studied in solutions in which it demonstrates a (quasi)reversible behavior at bare electrode surfaces, THF + TBAPF<sub>6</sub> and AN + TEACl. The standard redox potential of this species belongs to the range of the electroactivity of immobilized TcCl<sub>2</sub> centers (where the matrix is in its non-conducting state) so that the electron charge has to be transported via stepwise redox reactions between neighboring centers inside the film. The combination, solute reactant + film, results in a greater CV current compared to the response of the film in background solution or of the solute species at the bare electrode surface. This current for THF solution even exceeds the sum of separate currents for

the film and the reactant. This finding is attributed to a catalytic effect of solute species as redox intermediators for the transformation of immobilized electroactive centers leading to a greater degree of the film reduction. The presence of solute TcCl<sub>2</sub> species results in a much greater stability of immobilized centers (compared to the corresponding reactant-free solution), both in the course of CV with the passage of the range of their response and in experiments with the film holding at the potential within this range. This holding leads to an almost constant current related to the reaction of solute species at the film/solution interface. Our estimate shows that immobilized centers undergo above 10,000 reversible transformations (without an observed tendency to the degradation) to ensure the passage of this current. The conclusion has been drawn that immobilized TcCl<sub>2</sub> centers are able to serve as sufficiently stable redox intermediators for the electron charge transport across the film, a prerequisite for the catalytic applications of such films.

**Keywords** Conducting polymer · Modified electrode · Redox intermedialtor · Reaction kinetics

### Abbreviations

AN	acetonitrile
THF	tetrahydrofuran
Cp	cyclopentadienyl, C <sub>5</sub> H <sub>5</sub>
Cp'	cyclopentadienyl radical, C <sub>5</sub> H <sub>4</sub>
Fc	ferrocene, Cp <sub>2</sub> Fe
TcCl <sub>2</sub>	“titanocene” = bis(cyclopentadienyl)titaniumdichloride, Cp <sub>2</sub> TiCl <sub>2</sub> or its radical CpCp'TiCl <sub>2</sub>
PPy	polypyrrole
Tc3Py	titanocene-propyl-pyrrole, Cl <sub>2</sub> TiCpCp'(CH <sub>2</sub> ) <sub>3</sub> NC <sub>4</sub> H <sub>4</sub>
p(Tc3Py)	polymer obtained from Tc3Py
TBAPF <sub>6</sub>	tetrabutylammonium hexafluorophosphate
TEACl	tetraethylammonium chloride

Dedicated to Zbigniew Galus on the occasion of his 70th birthday.

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## Introduction

Metallocenes (*bis*-cyclopentadienyl complexes,  $Cp_2MX_2$ ) of group 4 are well known as homogeneous catalysts of olefin polymerization [1, 2] and various organic reactions [3, 4, 5, 6]. Their immobilization inside a porous solid matrix might open the prospects for the *supported molecular catalysis* [7, 8]. Such systems promise important merits compared to their homogeneous analogues, such as easy separation from the reaction products, diminution of catalyst losses, environmental factors, etc.

Keeping it in mind we have developed recently a procedure based on electropolymerization in acetonitrile (AN) of a monomer (**Tc3Py**) containing two functional groups, pyrrole (**Py**, functionalized at a nitrogen atom) and titanocene dichloride ( $TcCl_2 = CpCp'TiCl_2$ ) linked by an aliphatic (propyl) chain [9]. The conducting polymer films thus obtained (**pTc3Py**) possess (after their transfer to a monomer-free solution of the background electrolyte, TBAPF<sub>6</sub>) a redox activity in two intervals of potential corresponding to that of the polypyrrole matrix (positive potentials in our reference scale) and that of the response of pendant  $TcCl_2$  centers (about  $-1.0$  V) [9, 10]. The matrix activity is stable during cycling and similar in several solvents, AN, dichloromethane and THF. In contrast, the response of immobilized  $TcCl_2$  complexes depends essentially on the solvent.

The most stable response of centers is observed in THF solutions in which the film may be subject to a series of cycles without a noticeable diminution of the activity (if the solution is thoroughly deoxygenated). However, a break between the series of cycles leads to a marked diminution of the response of centers [10, 11].

This gradual loss of the electroactivity of centers represents a potential problem for possible applications of these systems for their electrocatalytic applications. One should keep in mind that the polymer matrix is in its insulating state within this interval of potentials. Therefore, the transport of the electronic charge between the reacting centers and the electrode has to be realized by the set of charge-transfer reactions between the neighboring  $TcCl_2$  centers. This means that the centers near the electrode surface have to pass the whole charge needed for the reaction of solute species, i.e. these complexes have to function as very stable and reversible redox centers.

In the actual study we present the first results for reactions of solute reactants at the surface of a **p(Tc3Py)** film. The species chosen for this aim, ferrocene (**Fc**) and titanocene dichloride ( $TcCl_2$ ), react at the *bare* electrode surface (Pt or glassy carbon) in a *reversible* manner (in the chosen solutions) so that the deposition of the film *cannot catalyze* these reactions. Therefore, this study was oriented to check whether both components of the film, the polypyrrole matrix and immobilized  $TcCl_2$  centers, are able to serve as *stable transmitters* of the

electronic charge between the reacting species and the electrode.

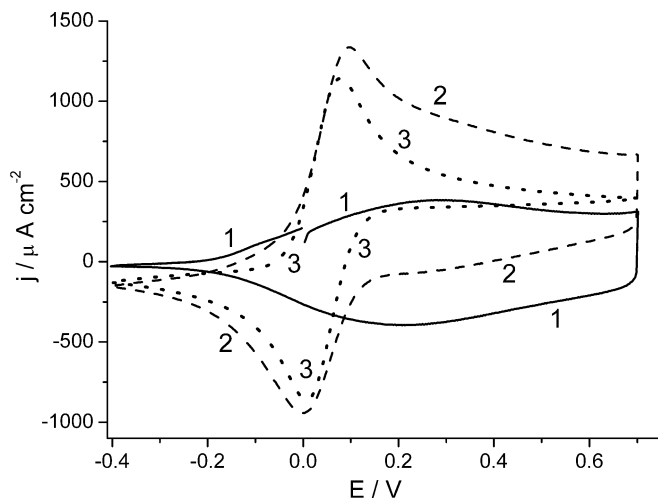
A positive answer to this question was intuitively expected for **Fc** while the result was quite unclear for the  $TcCl_2$  reaction, in view of the above mentioned gradual loss of the activity of immobilized centers.

## Experimental

All electrochemical measurements were carried out with the use of Autolab PGSTAT30 (Ecochemie, The Netherlands) in a conventional, single compartment cell with a Pt wire as a counter electrode (CE) and Ag/0.01 M  $AgNO_3 + 0.1$  M TBAPF<sub>6</sub> in  $CH_3CN$  (AN) double junction reference electrode (RE). All potentials in the paper are related to this RE. The procedure of the film deposition and the study of its redox activity have been described in refs [9, 10]. Polymerization of **p(Tc3Py)** films on a glassy carbon or Pt disc (surface areas,  $0.07$  cm<sup>2</sup> and  $0.005$  cm<sup>2</sup>, correspondingly) was performed potentiostatically (deposition charge,  $25$  mC/cm<sup>2</sup>) at about  $0.74$ – $0.76$  V from  $1$  mM monomer solution in AN +  $0.1$  M TBAPF<sub>6</sub> as described in ref [10]. After deposition the film was taken out from the monomer solution and rinsed with solvent in which the further measurements were planned to be realized. After the transfer to THF solution the film was activated by cycling in the range of the matrix activity ( $-0.4$  V up to  $0.7$  V) until a stable response was obtained. After this the cycling was extended to the whole potential range including that of the response of Tc centers,  $-0.4 \rightarrow 0.7 \rightarrow -1.4$  V  $\rightarrow -0.4$  V. For chloride solutions in AN, cycling was limited to a more narrow range, between  $-0.6$  V and  $-1.4$  V ( $-1.5$  V in the cases where the  $TcCl_2$  reduction peak was shifted significantly in the negative direction), because of an irreversible degradation of the matrix under the influence of chloride within the potential range of the matrix electroactivity starting from about  $0$  V [12].

The studies of reaction kinetics were performed in solution, THF or AN +  $0.1$  M TBAPF<sub>6</sub> or  $0.2$  M TEACl, with additions of **Fc** or  $TcCl_2$  (in the range of  $1$  mM). For the sake of comparison we used **Fc** and  $TcCl_2$  reactions at the bare Pt electrode as well as response of the film in the above background solution.

The salts, TBAPF<sub>6</sub> (Fluka) and TEACl (Aldrich), were dried at  $80$  °C for several hours prior to the use. THF (AnalytiCals, Carlo Erba) stabilized by hydroquinone was distilled over metallic Na + benzophenone (Merck). AN for polymerization was of spectrophotometric grade  $99.5\%$  (Aldrich), with initial water content  $< 0.03\%$ . AN for CV studies of the film in a monomer-free solution was HPLC grade (Carlo Erba) with initial water content  $< 0.02\%$ , distilled before use. All solutions were thoroughly deaerated by vacuum pumping and subsequent filling with dry argon prior to the experiments. The oxygen removal was controlled by



**Fig. 1** CV responses of the p(Tc3Py) film in background solution, AN+0.1 M TBAPF<sub>6</sub> (solid curve 1), and with addition of about 1.5 mM Fc (dashed curve 2), in comparison with the curve for the same Fc solution at the bare Pt electrode (dotted curve 3). Scan rate 100 mV/s

measuring CV in the background electrolyte (absence of the oxygen reduction wave at about  $-1.3$  V).

## Results

### Ferrocene in AN + TBAPF<sub>6</sub> solution

Fc is a well known reversible reactant at bare electrode surfaces for various solution compositions including a background electrolyte in AN (curve 3 in Fig. 1). Its standard potential,  $E^\circ = 0.042$  V (determined from the potentials of anodic and cathodic peaks), is within the range where the polymer matrix is in its oxidized state,

even though the degree of charging and correspondingly its electronic conductivity are relatively low. Therefore, one could expect that solute Fc molecules should react at the film/solution interface of the polymer-coated electrode, with the electron charge transport from the electrode across the film.

In accordance with these predictions we have observed curve 2 in Fig. 1 corresponding to a superposition of the responses of the polymer matrix (curve 1) and the solute Fc at the bare electrode (curve 3). Both peaks for curve 2 are slightly shifted to higher potentials, expectedly because of greater ohmic losses inside the film.

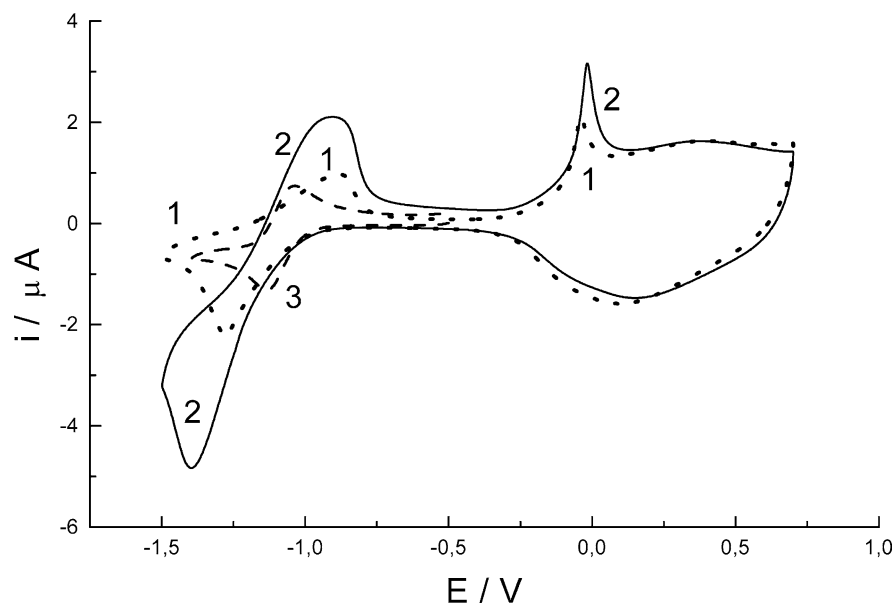
This means that the Fc reaction remains reversible at the film-coated electrode, owing to the electronic charge supply along the polymer matrix between the electrode and the reaction sites.

### Titanocene dichloride (TcCl<sub>2</sub>) in THF + TBAPF<sub>6</sub> solution

According to our earlier studies [9, 10, 12] the TcCl<sub>2</sub> electroreduction is partially or completely irreversible electrochemically for most solution compositions, both for solute species and immobilized complexes. A quasi-reversible behavior has only been observed for THF with a background electrolyte and in the presence of a sufficiently high concentration of a chloride salt (in AN or DMF). This is why the actual study was performed for Tc3Py film in contact with these solutions.

As one can see from Fig. 2, the presence of the species TcCl<sub>2</sub> which are electroactive in the same potential interval as immobilized centers results in a strong increase of the reduction and oxidation peaks in the course of CV with passage of the Tc potential range (curve 2), compared to the response of the same film in the background THF + 0.1 M TBAPF<sub>6</sub> solution (curve 1). The straight-

**Fig. 2** CV responses of the p(Tc3Py) film within the whole range of potentials in THF + 0.1 M TBAPF<sub>6</sub> (dotted curve 1) and with addition of 1 mM TcCl<sub>2</sub> (solid curve 2), in comparison with the curve for the same TcCl<sub>2</sub> solution at bare electrode (dashed curve 3). Scan rate 100 mV/s. Platinum electrode



forward interpretation of this observation is a reaction of solute  $\text{TcCl}_2$  species at the surface of the film which results in an additional contribution to the faradaic current.

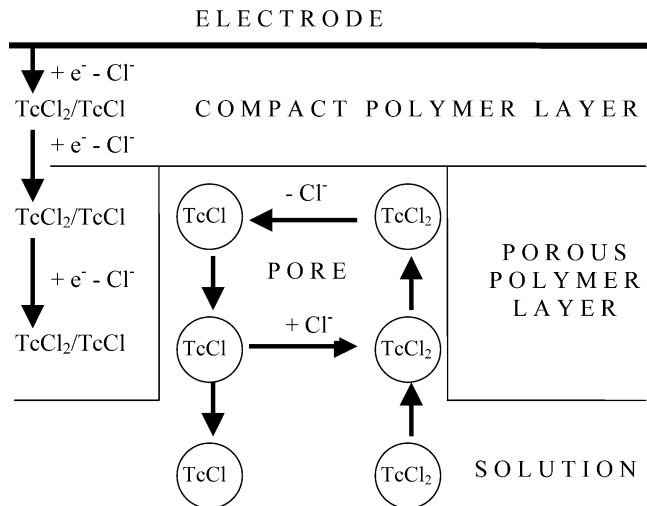
However, the phenomenon is more complicated, as is shown by comparison with curve 3 corresponding to the reduction of solute  $\text{TcCl}_2$  species at the bare electrode surface. The latter process is controlled by diffusion so that the presence of the film cannot increase the amount of solute molecules which can reach the surface within the CV peak (our recent STM studies have shown that the external surface of the film is very flat, with a roughness height at the 10 nm scale which cannot influence the diffusion flux to the surface). Therefore, the observed great increase of the faradaic current for the film (curve 2) compared to that for the bare electrode (curve 3) must be attributed to the reduction current due to  $\text{TcCl}_2$  centers immobilized inside the film.

A more detailed analysis reveals an even more surprising feature. The current for the combination "film +  $\text{TcCl}_2$ " (curve 2) is *stronger than the sum* of the currents for "film" (curve 1) and " $\text{TcCl}_2$  without film" (curve 3).

For explanation of this apparent paradox one should take into account that the rate of charge transport across the film is sufficiently slow since the matrix is in its non-conducting state so that the reduction of centers in the background solution is realized solely by redox reactions between the neighboring  $\text{TcCl}_2$  centers. As a result, only a fraction of the centers located not far from the electrode surface (less than one half of the film thickness for 100 mV/s) is subject to the reduction in the background solution (curve 1).

The situation changes in the presence of solute  $\text{TcCl}_2$  species which can penetrate deeply inside the film owing to its porous nature (but not up to the metal surface which is covered by a thin but compact polymer layer preventing the approach of solute species to the metal surface [13]). The rate of this diffusion-type movement is much faster than the rate of the above film-reduction transport. Therefore, these solute species react with reduced centers near the external surface of this *compact layer* inducing, on the one hand, an additional charge transport across the compact layer and, on the other hand, the diffusion of reduced solute molecules along the pores to the solution. But on the way there these species may react with immobilized centers which have not been reduced as yet due to a slow transport across the film. This regenerates solute molecules in their initial (oxidized) state which can diffuse again the surface of the compact layer.

As a result, these solute species function as a redox mediator, effectively accelerating the charge-propagation rate across the film, i.e. increasing the charge of the film reduction for curve 2 compared to curve 1 and correspondingly to a greater total reduction charge for this case compared to the sum of the individual components. In a certain meaning one may consider this phenomenon as a catalysis of the film reduction by the solute redox couple.



**Scheme 1** Reduction process of solute and immobilized  $\text{TcCl}_2$  complexes at the film-coated electrode

The whole process can be represented by Scheme 1.

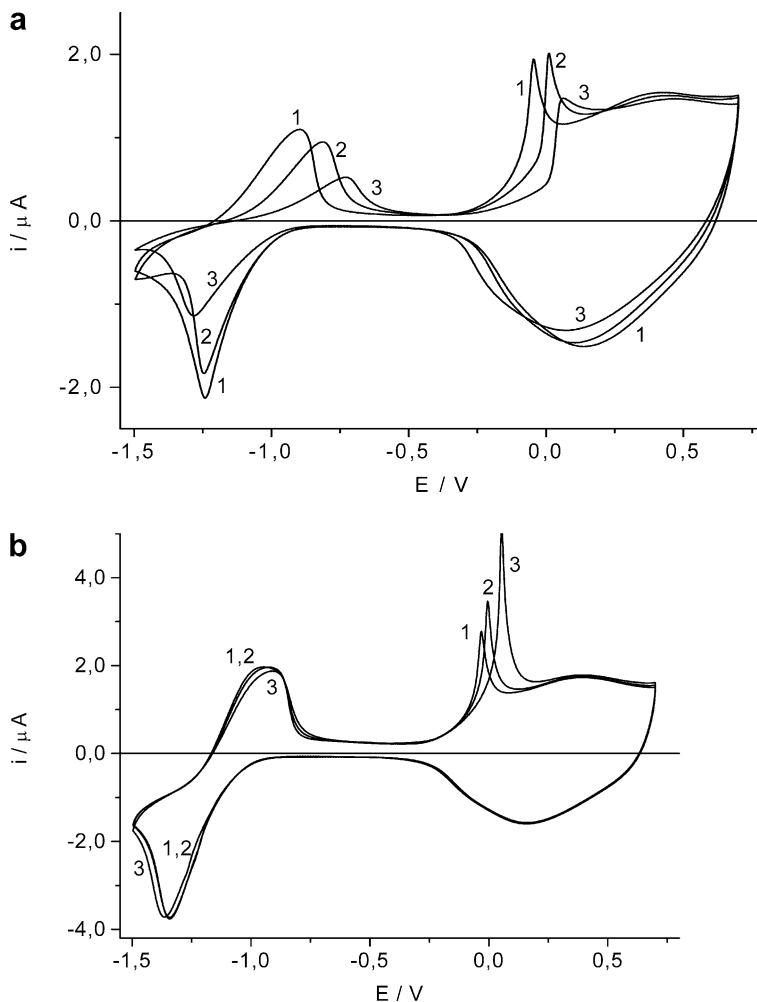
One can also note a drastic increase of the peak separation (difference between the reduction and the reoxidation peak potentials) for the film-coated electrode, about 400 mV for the background electrolyte (curve 1) and even about 500 mV in the presence of solute  $\text{TcCl}_2$  species (curve 2), compared to the quasi-equilibrium CV curve for the bare electrode, 100 mV (curve 3). On the other hand, the mean potential for this cyclic transformation (reduction–reoxidation) does not change significantly, being about 1.08 V for curves 1 and 3 and slightly more negative, -1.15 V, for curve 2. These features arise from a high resistance to charge transport (both electron and ion) inside the film while the thermodynamics of the process (i.e. the mechanism) remains unchanged.

The addition of solute  $\text{TcCl}_2$  molecules to the background THF solution also leads to another interesting effect, a significant increase in the stability of immobilized titanocene centers.

In the pure background solution (after its careful deoxygenation) their redox response may be stable within a series of cycles [10]. However, the activity gradually vanishes during a sequence of such series. The electroactivity of the centers is also lost if the potential of the electrode is held at a sufficiently negative potential (after the passage of the reduction peak of immobilized centers).

The latter effect is demonstrated in Fig. 3a. The film was subject to a five-step treatment, each of these steps including three cycles over the whole potential range, between 0.7 V and -1.5 V (i.e. 15 cycles as a whole). Series 1, 3 and 5 corresponded to the standard continuous cycling (Fig. 3a shows the *second* cycle in each of these series, curves 1, 2 or 3, correspondingly). In contrast, in the second cycle of series 2 and 4 the potential sweep was interrupted at a potential within the  $\text{TcCl}_2$  reduction range, -1.25 V, the film was kept at this

**Fig. 3 a** Effect of the film holding in the negative potential range on the shape of the subsequent voltammogram in THF + 0.1 M TBAPF<sub>6</sub> solution. Five series with three cycles in each series. Series 1, 3 and 5: in each series three cycles were performed continuously within the whole potential range, between 0.7 V and -1.5 V, with -0.4 V as a starting and final potential. The second cycle of series 1, 3 or 5 is shown in Fig. 3a as curve 1, 2 or 3, correspondingly. Series 2 and 4: again three cycles within the same potential range but the potential sweep in the course of the second cycle of each series was interrupted at -1.25 V and the potential was kept at this value for 50 s (series 2) or 100 s (series 4), then the potential sweep was continued. Scan rate 100 mV/s. **b** Effect of the film holding in the negative potential range on the shape of voltammogram in THF + 0.1 M TBAPF<sub>6</sub> solution with addition of 1 mM TcCl<sub>2</sub>. The same treatment as in Fig. 3a but with the holding potential equal to -1.3 V, in view of a stronger negative shift of the film reduction wave for this solution, see Fig. 2. Scan rate 100 mV/s



potential for 50 s (series 2) or 100 s (series 4), and then the sweeps were continued.

In Fig. 3a one can see two pronounced effects of this holding at a negative potential:

- Both the reduction and reoxidation peaks of immobilized centers diminish markedly after this holding, much more strongly than in a similar experiments without holding.
- The resistance of the polymer matrix increases significantly during the holding, see the discussion in ref [10] for more details.

Our actual study of the film-coated electrode in contact with the TcCl<sub>2</sub>-containing solution in THF (again, with its careful deoxygenation) shows that this degradation process is strongly inhibited. In particular, the redox response of immobilized centers remains intact even after realization of a series of CV cycling procedures.

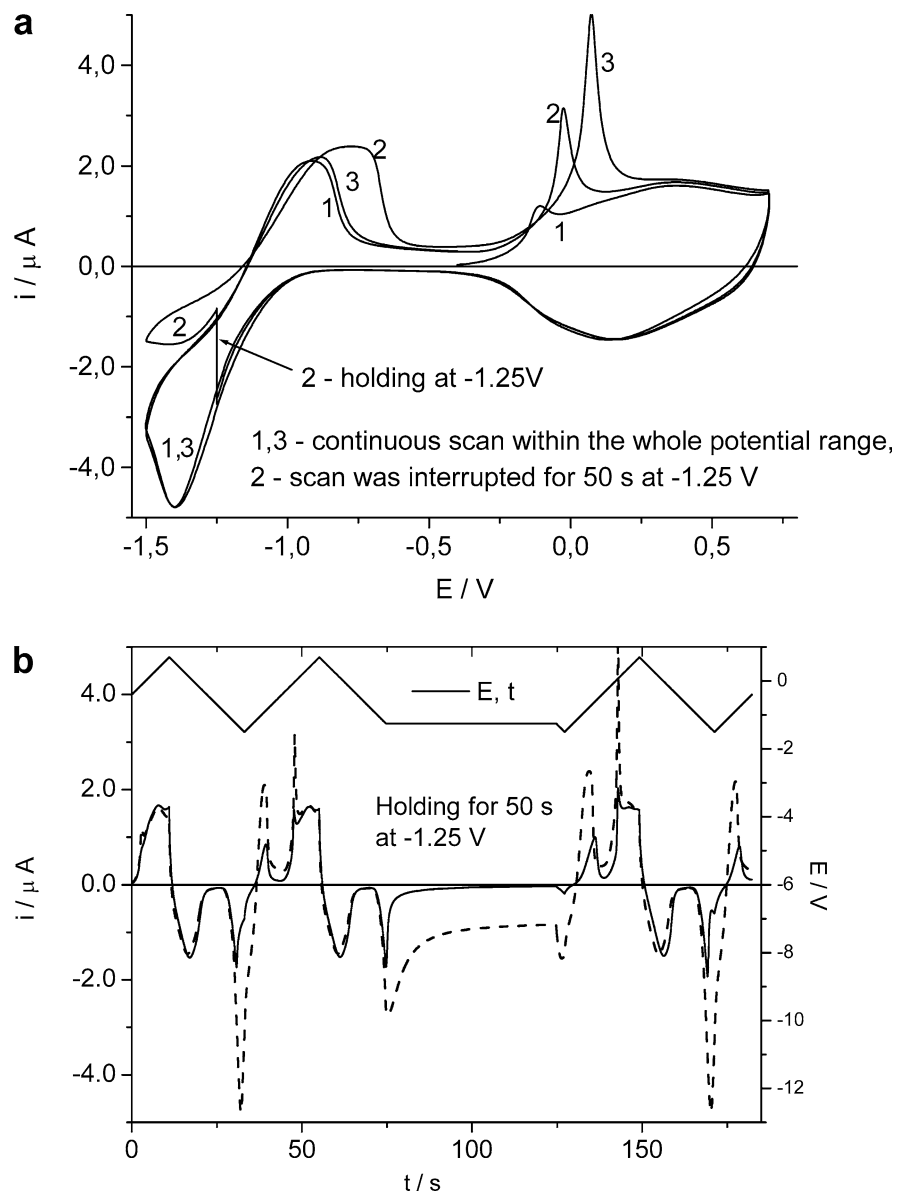
A much greater stability of the response of immobilized TcCl<sub>2</sub> centers in the presence of solute titanocene dichloride species is also observed if the film is subject to the holding at a TcCl<sub>2</sub> reduction potential for an extended time. Figure 3b demonstrates the results of the five-step treatment similar to that in Fig. 3a for the

background solution. In this case there is practically no diminution of the electroactivity of centers after the holding. As for the increase of the resistance of the polymer matrix resulting in a shift of the oxidation peaks to higher potentials, it is almost absent for the reoxidation peak of TcCl<sub>2</sub> at about -0.9 V, compare Fig. 3a.

The next experiment was carried out to see whether the TcCl<sub>2</sub> centers inside the film are able to function as a *stable* and *reversible* redox intermediary for the reduction process of solute species. Figure 4a presents a voltammogram for three cycles (without a break between them) over the whole potential range, with an interruption of the potential sweep at a negative potential, -1.25 V, within cycle 2. Then, the potential was kept constant for 50 s, with the registration of the current versus time.

The chronoamperometric curve for the whole three-cycle procedure is given in Fig. 4b, together with the similar curve measured for the film in background solution (without solute TcCl<sub>2</sub> species). Their comparison again confirms a much greater intensity of all peaks (reduction, reoxidation and prepeak) as well as a great stability of the film response to holding in the negative

**Fig. 4 a** Voltammogram of the film-coated Pt electrode in 1 mM  $\text{TcCl}_2 + 0.1 \text{ M TBAPF}_6 + \text{THF}$  solution. Three cycles in the complete range, between 0.7 V and  $-1.5 \text{ V}$ . During cycle 2 the sweep was interrupted at  $-1.25 \text{ V}$ , the potential was kept constant for 50 s, and then the sweep was continued. Scan rate 100 mV/s. **b** Potential and current versus time dependences during the three-cycle procedure with holding (see Fig. 4a), for the background solution, 0.1 M  $\text{TBAPF}_6$  in THF (solid curve) and with addition of 1 mM  $\text{TcCl}_2$  (dashed curve). Scan rate 100 mV/s



potential range owing to the presence of the solute reactant. A new observation is a drastic difference in the chronoamperometric curves during the holding period: the current vanishes rapidly in the background solution while it approaches a constant value in the presence of solute  $\text{TcCl}_2$  species.

Since the compact polymer layer near the electrode surface prevents a reaction of solute reactants at the metal surface (see Scheme 1) this direct current must be ensured by redox transformations (reduction and reoxidation) of immobilized centers inside the film.

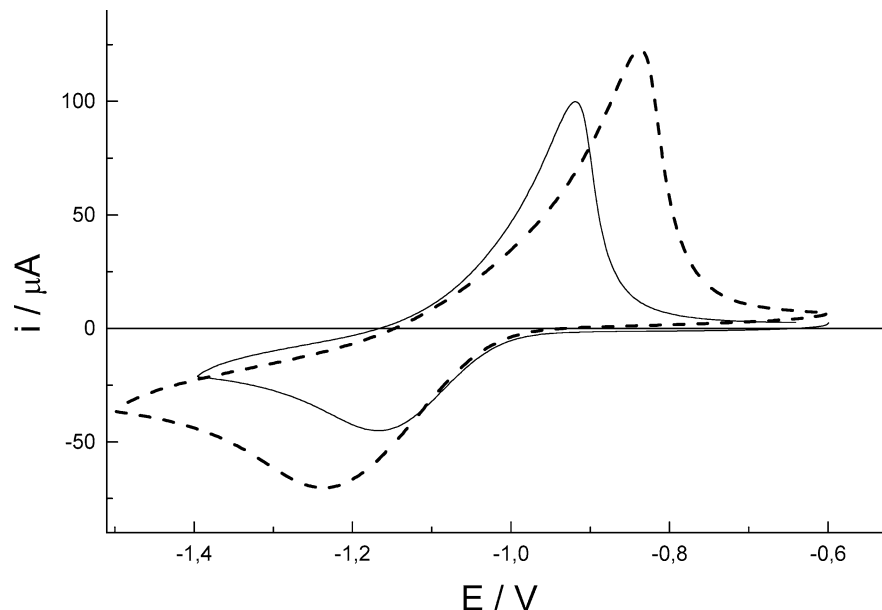
One must keep in mind that the polymer matrix is in its non-conducting state within this potential range. Therefore, the charge transport inside the film (in particular, across its compact layer) can only be realized by a set of redox reactions between the *neighboring* immobilized centers, or between the electrode and the adjacent  $\text{TcCl}_2$  center, at a distance of the nanometer scale.

The volume of the monomer,  $\text{Tc3Py}$ , in its crystalline state, about  $400 \text{ \AA}^3$ , gives a *crude* estimate for the size of this molecule,  $7\text{--}8 \text{ \AA}$ , and for the surface area at the electrode occupied by a single center,  $50\text{--}60 \text{ \AA}^2$ . It implies that *the whole reduction charge* must pass through the centers within a *monolayer* of the monomer units at the metal surface. Therefore, we can estimate the number of redox transformations,  $n$ , of these centers within the first monolayer to pass the total reduction charge per unit surface area,  $q$ :

$$n = q / (F \Gamma), \quad \Gamma = (N_A A)^{-1} \quad (1)$$

Here,  $F$  is the Faraday constant,  $\Gamma$  is the “monomer surface density” (number of its moles per unit surface area),  $N_A$  is Avogadro’s number, and  $A$  is the surface area per monomer unit. The above value for  $A$  allows one to obtain an estimate for the product,  $F\Gamma \approx 0.03 \text{ mC/cm}^2$ .

**Fig. 5** Stabilized CV responses of the p(Tc3Py) film within the whole potential range in 0.2 M TEACl+AN (solid curve) and in the same solution with addition of 1 mM TcCl<sub>2</sub> (dashed curve). Carbon electrode. Scan rate 100 mV/s



The integration of the chronoamperometric curve in Fig. 4b for the TcCl<sub>2</sub> containing solution gives 12.8 mC/cm<sup>2</sup> for the total reduction. Then, Eq. (1) shows that each center is subject to about 400–450 redox transformations. One should take into account that the current does not demonstrate any tendency to vanish by the end of the holding period in Fig. 4b so that the real ability of the centers to undertake this “catalytic turnover” must be much higher.

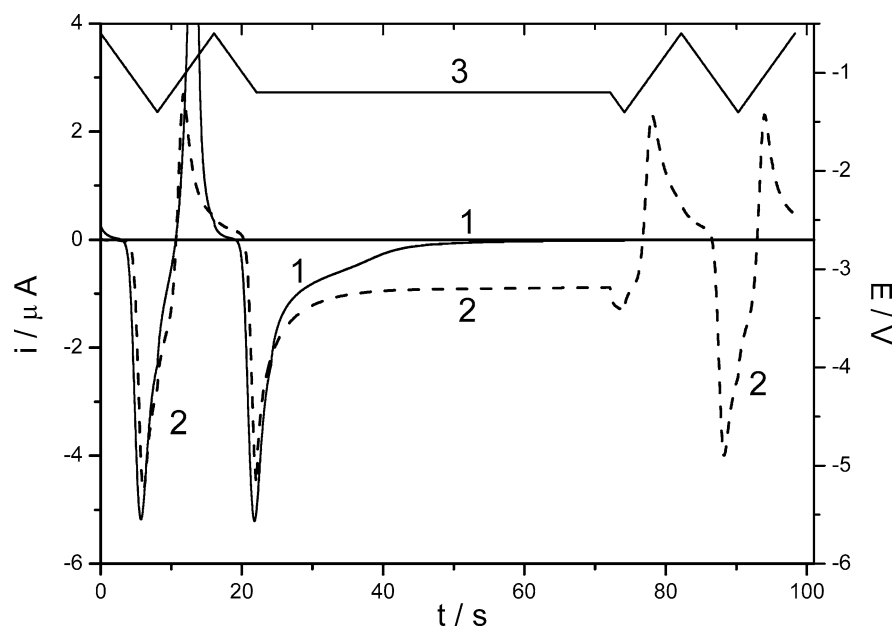
#### Titanocene dichloride (TcCl<sub>2</sub>) in AN+TEACl solution

Another possibility to obtain a pseudo-reversible CV response of solute TcCl<sub>2</sub> species is to carry out the

process in a chloride-containing solution, e.g. in AN. The presence of chloride anions influences the dissociation process of anion radicals generated by the electron transfer:  $\text{TcCl}_2^- \rightarrow \text{TcCl} + \text{Cl}^-$ , increasing the concentration of non-dissociated complexes so that the reoxidation in the course of the back scan takes place near the same potential.

We have found recently [11] that the redox activity of immobilized TcCl<sub>2</sub> centers in such a chloride-containing medium is also rather stable, in contrast to that in the background solution. At the same time, the presence of chloride in solution results in a rapid degradation of the polymer matrix for the potential range above 0 V [12]. Since the reduction of solute TcCl<sub>2</sub> molecules takes place at sufficiently negative potentials this feature does not

**Fig. 6** Current and potential time dependences for the p(Tc3Py) film during the three-cycle potential sweep, with holding the potential equal to -1.2 V for 50 s during cycle 2, see legend to Fig. 4a, in 1 mM TcCl<sub>2</sub>+0.2 M TEACl+AN solution (dashed curve 2 for current and curve 3 for potential). The film response in the same solution without TcCl<sub>2</sub> is given by solid curve 1. Scan rate 100 mV/s



represent an obstacle to the study of this reaction at the electrode modified by the p(Tc3Py) film.

Figure 5 shows CV curves (after several initial cycles) for the film (deposited at the carbon electrode) in contact with the chloride solution in AN and with addition of 1 mM TcCl<sub>2</sub>. The positive limit of the scan is limited to -0.6 V to avoid the degradation of the matrix at positive potentials. In both cases the response is sufficiently stable. The presence of the solute reactant increases again the redox current but this time the effect is small.

We have also performed experiments with holding the film at the negative potential in the range of TcCl<sub>2</sub> reduction. Fig. 6 presents chronoamperometric curves for the three-cycle procedure with holding the potential constant within the TcCl<sub>2</sub> reduction range in cycle 2, already discussed for the THF solution (see Fig. 4a and b). Similar to the latter case, the response of immobilized centers is restored almost completely in continuous cycle 3 (compared to cycle 1). As for the holding period, one can see again that the current in the chloride solution vanishes after the "relaxation period" while it approaches a stabilized value in the presence of solute TcCl<sub>2</sub> species. Compared to curves in THF solution (Fig. 4b) the "relaxation period" corresponding to the charging the immobilized centers inside the film is markedly shorter while the peak current is higher, due to a faster charge transport across the film in contact with AN solution. As for the direct current in the presence of the solute reactant its value is higher for the AN solution than for the THF one. However, the total reduction charge is about the same, 12.4 mC/cm<sup>2</sup> for AN and 12.8 mC/cm<sup>2</sup> for THF solutions.

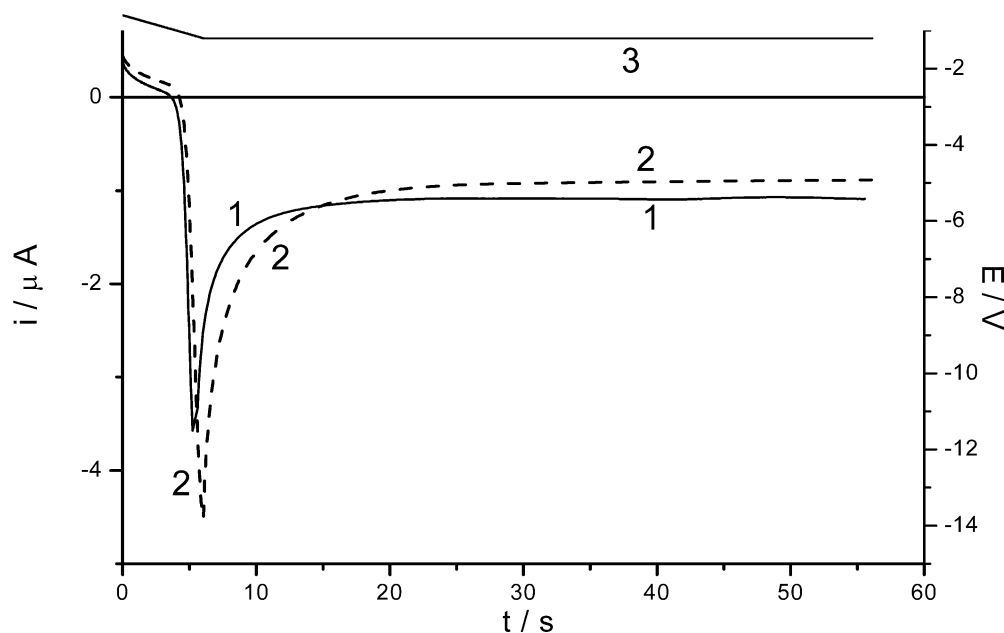
We will discuss this dependence of the charge transport rate across the film and at its interface on the composition of the solution in another paper.

Figure 7 presents a comparison of chronoamperometric curves (linear sweep up to a negative potential limit, -1.2 V for the film or -1.15 V for bare electrode, followed by the electrode holding at this potential for 50 s) for two electrodes, bare Pt and the same electrode coated with the p(Tc3Py) film, in contact with the 1 mM TcCl<sub>2</sub> solution in AN. The peak current in the latter case is significantly greater and its diminution is slower than that for bare Pt, due to a contribution from the reduction of immobilized TcCl<sub>2</sub> centers inside the film. In contrast, the stabilized reduction current is slightly higher for the bare electrode, 1.09  $\mu$ A versus 0.89  $\mu$ A (this difference is rather small but well beyond experimental errors). This effect may originate from at least two causes:

- A part of the film (below 20% of the total surface area) is not sufficiently electroactive/conducting in this range of potentials so that it cannot serve for mediated catalysis.
- The whole film is fully active but there is a significant resistance to the electron charge transport across the film, comparable with that of the diffusional transport of the electroactive species in the solution including that along the pores inside the film. Since the current is determined by the total resistance which represents the sum of the resistances of all individual transport steps, in the external diffusion layer of the solution, inside the pores of the film, at the film/solution interface and inside the compact polymer layer (see Scheme 1) the contribution of all components related to the film does not exceed 20% of the total value.

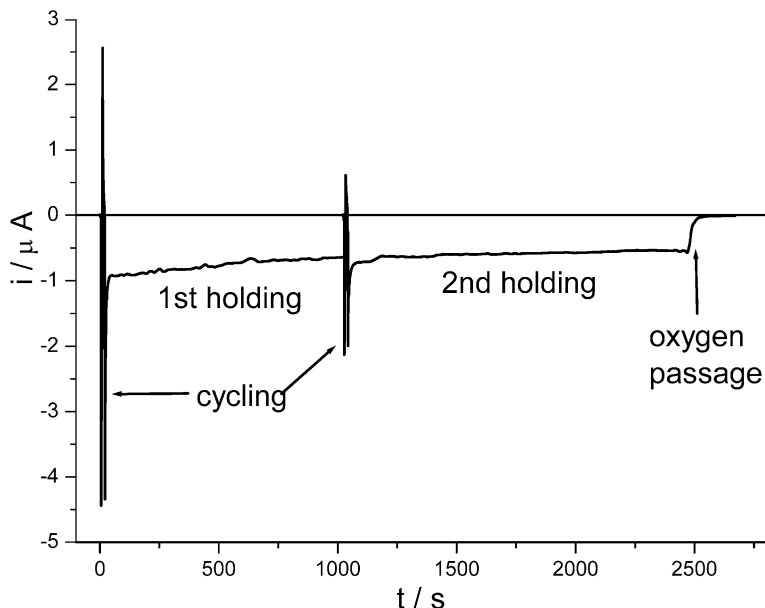
The distinction between these two possibilities might be made with the use of a technique allowing one to modify in a controllable manner the "external" transport, e.g. RDE but it must be compatible with a

**Fig. 7** Current (curves 1, 2) and potential (curve 3) time dependences for bare Pt (solid curve 1) and the same electrode coated with p(Tc3Py) film (dashed curve 2) in 1 mM TcCl<sub>2</sub> + 0.2 M TEACl + AN solution during the potential sweep (scan rate 100 mV/s) from -0.6 V to -1.15 V (for Pt) or -1.2 V (for film) followed by holding the potential at this value for 50 s





**Fig. 8** Chronoamperometric curve for the film-coated electrode in 1 mM  $\text{TcCl}_2 + 0.2 \text{ M TEACl} + \text{AN}$  solution during a multi-step procedure: cycling within the potential range,  $-0.6 \text{ V}$ ,  $-1.4 \text{ V}$ , then holding the film at  $-1.2 \text{ V}$  for 1,000 s, a new CV series, the second holding period of about 1,500 s, and finally degradation of the film under the action of dissolved oxygen



strict deoxygenation of the solution during the measurement.

To check the long-time stability of the response of the immobilized centers we subjected the film-coated electrode to a procedure similar to that in Fig. 6 but with an extended holding time. The results for two such periods of exposure for the same film, about 1,000 s and 1,500 s, are given in Fig. 8. The activity of centers inside the film was checked by cyclic voltammetry (see Fig. 5 for conditions) before and after both periods.

One can observe a gradual diminution of the faradaic current during this long period of about 2,500 s but the loss is very slow, from  $0.92 \mu\text{A}$  initially to  $0.54 \mu\text{A}$  at the end. A similar (about two times) diminution of the electroactivity of immobilized centers is also shown by the cyclic voltammetry.

The total reduction charge during the whole treatment was about  $1644 \mu\text{A}$ , i.e.  $329 \text{ mC/cm}^2$ . If this charge density is inserted into Eq. (1) it allows us to get a much higher value for the number of redox transformations of immobilized centers near the electrode surface:  $n \approx 11,000$ . It should be kept in mind that the current has not vanished by the end of the observation period so that this value could obviously be further increased by a longer exposure.

In the above reasoning it was assumed implicitly that all measured current correspond to the reaction of solute species at the *film/solution interface*, i.e. that the electrode surface is completely covered by the polymer phase preventing a direct reaction of solute species at this surface. To verify this assumption we have performed control experiments.

First, oxygen was allowed to enter the cell. Since the reduced  $\text{TcCl}_2$  centers react immediately and irreversibly with this agent the reaction of solute  $\text{TcCl}_2$  species stopped at once (Fig. 8).

Second, we have checked that after this degradation the film is still left at the electrode surface. For this the

film-coated electrode was rinsed and transferred into the background electrolyte solution,  $\text{TBAPF}_6 + \text{AN}$ , without  $\text{TcCl}_2$  or  $\text{TEACl}$ . The CV study in this solution has shown a response of the polymer matrix (with a small loss compared to that in its initial state).

Finally, the electrode was returned to the solution,  $1 \text{ mM TcCl}_2 + 0.2 \text{ M TEACl} + \text{AN}$ . CV performed within the potential range from  $-0.6 \text{ V}$  to  $-1.4 \text{ V}$  did not show any response of immobilized centers, even after all oxygen had been removed from the cell.

This altogether allows us to conclude that the film completely blocks the electrode surface so that solute electroactive species cannot react directly at the metal surface and the only possible reaction pathway corresponds to the process mediated by immobilized centers presented in Scheme 1.

## Conclusions

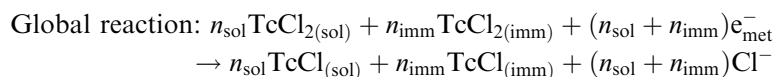
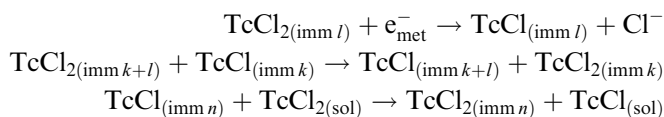
This paper presents the first results on the kinetics of redox reactions of solute species at the surface of the electrode coated with a conducting polymer film functionalized with immobilized titanocene dichloride ( $\text{TcCl}_2$ ) centers. For this study we have chosen the reactants whose redox response corresponds to two different intervals of the film electroactivity, Fc in the matrix range and  $\text{TcCl}_2$  in the range of immobilized centers. Both species were studied in the solutions where they demonstrate a (quasi-)reversible response at the bare electrode surface.

At the potential of the Fc oxidation the polymer matrix is in its oxidized state. It is well known that even a short-length aliphatic N-substitution of pyrrole (e.g. N-methyl pyrrole) leads to polymer films having a much lower electronic conductivity, several orders of magnitude lower than that of the non-substituted PPy [14]. The similarity of electrochemical properties of our

polymer with those of poly(*N*-alkyl pyrrole) allows us to assume that the matrix conductivity in its oxidized state should not be too low, at least the films under study behave in cyclic voltammetry with usual scan rates as a perfect capacitor (proportionality between the CV response and the scan rate), i.e. the charge transport across the film does not limit the oxidation or reduction process. Since the ohmic potential drop in the bulk solution is sufficiently small for our conditions (the current being in the interval of a few  $\mu\text{A}$  for Pt or a few tens of  $\mu\text{A}$  for a C electrode) we may assume that the electron charge transport across the film during the reaction of solute reactant (Fc) at the film surface will not be the limiting step. Since the surface area of the film/solution interface is high due to the film porosity it was natural to expect that the Fc oxidation at this modified electrode should be analogous. This prediction of a reversible behavior has been confirmed in our experimental study.

The situation seemed to be less evident for the reduction of solute  $\text{TcCl}_2$  species at the film surface, in view of the gradual decrease of the response of immobilized titanocene dichloride centers even in the most favorable conditions, if the film was put under the action of a potential within the range of the  $\text{TcCl}_2$  electroactivity. Surprisingly, we have revealed that the presence of  $\text{TcCl}_2$  species in solution increased markedly the stability of the response of immobilized centers including consecutive series of cycles or/and holding at a negative potential. Moreover, we have observed a *direct current* related to the reaction of solute species at the film-coated electrode.

Since the polymer matrix is in its non-conducting state in this range of potentials while the surface of the electrode itself is blocked by the compact polymer layer preventing the direct reaction of solute species at this surface, the electronic charge from the electrode for the reduction of these species as well as  $\text{TcCl}_2$  centers in the film must be supplied by means of local exchange reactions between the neighboring immobilized centers. As a whole, the process can be represented by a scheme:



Here, index (sol) means a solute species, index (imm *k*) corresponds to a centre in the *k*th layer of the film.

We may conclude that immobilized  $\text{TcCl}_2$  centers are able to serve as a stable reversible intermedior for reduction of solute redox species. To function as such they must perform numerous reduction–oxidation cycles. The data of this study show that this turnover exceeds 10,000 for centers near the electrode surface, still without a complete degradation of these centers. This property represents a prerequisite for catalytic applications of such films.

These findings open the prospect that these immobilized centers can be used as supported catalysts for transformations of other solute reactants.

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