

Synthesis of titanocene containing conducting polymer films

M. A. Vorotyntsev, L. Roullier, E. Pousson, M. Casalta,
G. Boni, C. Moïse

UMR 5632 CNRS - LSEO, Université de Bourgogne,
Dijon, France; MV@U-bourgogne.fr

Conducting polymers represent an object of numerous studies in view of their unique combination of properties making them prospective for various applications. Most of them can be easily obtained in the form of films at the electrode surface by the oxidative electropolymerization in the solution of the corresponding monomer. This possibility is directly related to the high electronic conductivity of these materials within this potential range which allows the polymerization process to continue at the outer boundary of the film.

During the recent period there is a gradual shift of the research interest from the basic systems (polypyrrole, polythiophene and polyaniline) to their derivatives possessing a greater variety of their properties. In particular, first examples of films containing organometallic centers have been synthesized. These attempts are stimulated by the hope to create new immobilized catalysts and sensors.

These publications deal mostly with the derivatives of the iron and platinum groups of metals. The extension of these studies to other transition metals, in particular to those of groups IV-VI may open new prospects in this area since the corresponding organometallic complexes are well known as catalysts of numerous organic reactions in solutions and polymerization. We present here the first system of this kind where the polypyrrole film is modified by the titanocene dichloride centers, $Cp_2Ti(IV)Cl_2$ ($Cp = C_5H_5$).

The most reliable way to immobilize a molecular center inside a conducting polymer film always possessing a considerable porosity is provided by its chemical attachment to the polymer matrix. In our study it was achieved by the chemical synthesis of a new titanocene dichloride derivative, $TcRPy$, where one of the cyclopentadienyl ligands was functionalized with the pyrrolyl ring via an aliphatic chain ($Tc = CpCp^*TiCl_2$, $Cp = C_5H_5$, $Cp^* = C_5H_4$, $R = (CH_2)_3$, $Py = NC_4H_4$).

The redox properties of this derivative have been studied first in solutions of acetonitrile (AN), dichloromethane (DCM), or tetrahydrofuran (THF) at Pt electrode, with its comparison to the unsubstituted Tc. The reduction of Ti(IV) to Ti(III) is accompanied by a rapid loss of one of chloride anions which is replaced by the solvent molecule as a ligand in the complex. The subsequent reoxidation in strongly coordinating solvents (like AN) may only be possible at much more positive potentials while it is looking as an almost reversible process in THF and DCM. The titanocene dichloride (without pyrrole group) after its reduction had been known to be irreversibly hydrolyzed in the presence of water as well as to react with the dissolved oxygen. Moreover, the solubility of the modified monomer in AN or DCM is strongly reduced compared to that of pyrrole, the saturation concentration being about 1 mM.

These properties complicate the electrosynthesis of the

corresponding polymer films. In addition, the electronic conductivity of these films is much lower than that of polypyrrole so that one can notice a marked ohmic potential drop increasing parallel to the film thickness which shifts the wave of the monomer oxidation as well as the onset of the polymer redox charging in the course of the anodic scans of the potential. This effect is especially pronounced in THF, thus excluding this solvent from the possible media even for the studies of polymer redox properties.

Our study has shown that the most favorable results are obtained if the film synthesis is carried out in AN without adding water and thus modified electrode is transferred into DCM to study the redox properties of the polymer matrix and Tc centers. The films formed potenti- or galvanostatically or potentiodynamically give similar CV responses in the monomer free solution within the interval of the polymer activity, both in AN and DCM. Low solubility of the monomer leads to the necessity to use weak polymerization currents, e.g. $10-15 \mu A/cm^2$ for $i = const$. Besides, to obtain a pronounced redox response of the polymer matrix it is of crucial importance to avoid its overoxidation during the synthesis or the further cycling (in accordance with earlier results for other pyrrole films modified with transition-metal complexes [1-3]).

In these conditions we have observed high values of the "polymerization yield" defined from the ratio of the redox charge of the polypyrrole matrix and the polymerization charge during the synthesis, 5-8 %, which is close to that of native polypyrrole (4.5-8.5%) and exceeds the one of the polyalkylpyrroles (2.5-3.5%) [4]. The shape of this CV response corresponds to the "polypyrrole III" type[5] : the peaks are not especially pronounced, the hysteresis is small, CV curves are proportional to the scan rate (measured within the 20-200 mV/s interval). This result is in accordance with the conclusions by Heinze et al [6] since our AN solutions contained a sufficient amount of water to realize the polymerization and the synthesis potential was not especially low.

Redox transitions of titanocene groups immobilized inside the film can only be realized in DCM. The ratio of the Tc reduction charge during the first scan to that of the polymerization or to that of the polymer redox transformation depends on the sweep rate, v . For a sufficiently slow scan these charges are independent of v , the Tc reduction charge being 3-4 times greater than that of the polymer matrix oxidation, in conformity to the conventional "maximum charging degree" of the latter, 0.25-0.3. For higher scan rates the Tc reduction charge diminishes as $v^{-1/2}$. This dependence can be attributed to the incomplete film reduction because of a slow electron exchange between the neighboring Tc groups inside the film. Electron transport parameters have been estimated.

References

- [1] S. Cosnier, A. Deronzier, J.-F. Roland, J. Electroanal. Chem. 285 (1990) 133.
- [2] A. Deronzier, J.-C. Moutet, Coord. Chem. Rev. 147 (1996) 339.
- [3] Siant-Aman, M. Ungureanu, T. Visan, J.-C. Moutet, Electrochim. Acta 42 (1997) 1829.
- [4] A. F. Diaz, J. I. Castillo, J. A. Logan, W.-Y. Lee, J. Electroanal. Chem. 129 (1981) 115.
- [5] M. Zhou, J. Heinze, J. Phys. Chem. B 103 (1999) 8443.
- [6] M. Zhou, J. Heinze, J. Phys. Chem. B 103 (1999) 8451.