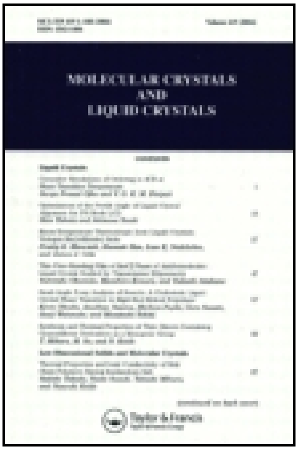

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INCLUSION OF METALLIC AGGREGATES IN ORGANIC CONDUCTING POLYMERS. A NEW CATALYTIC SYSTEM FOR THE H^+ REDUCTION.

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Abstract : Among the well-known organic conducting polymers, polythiophene and its derivatives have been shown to be remarkably stable in both their conducting and insulating states. Furthermore, they can be reversibly cycled between these two states in water. The use of metals complexes anions as electrolyte allows the doping of polythiophene with metal derivatives. Their further electrochemical reduction leads to the formation of metallic aggregates in the polymer . Thus, Ag and Pt clusters have been included in poly 3 methylthiophene : i-Ag clusters are mainly located along the polymer fibers and ensure the conductivity of this charged polymer, even in the cathodic range correspondint ot its neutral state; ii-Pt clusters are located near the surface of the polymer; iii-thus system shows a very high catalytic activity for the proton reduction in acidic medium (pH = 0, V = -0.4 V/SCE and J ∿ $200 mAcm^{-2}$ instead of $130 mAcm^{-2}$ with a platinized electrode). A remarkable stability is obtained, more than 170 hours (20 min with polypyrrole).

INTRODUCTION

A lot of work has been devoted to the physico-chemical properties of metallic clusters or aggregates, owing to their interesting applications in the field of catalysis[1]. The major problem encountered concerns the migration and the aggregation of the highly dispersed phase, which lowers the catalytic activity[2]. A partial answer has been given by the use of polymeric matrix instead of mineral support[3]. Another way to decrease this aggregation process involves the use of grafted electro-active films, which combine the two features of catalytic and electro-active sites[4]. In this regard, the inclusion of RuO_2[5] or of phthalocyanines[6] in polypyrrole, an organic conducting polymer , allowed the reduction of O_2 into H_2O_2. These new systems however possess low catalytic yield and poor stability.

We have recently shown the interesting properties of polythiophene and its derivatives as electro-active polymers[7]. Their high stability[8] and the possibility to dope them in water[9] make them goods candidates for the obtention of new catalytic systems. We thus report here the electro-chemical conditions allowing the inclusionof Ag and Pt aggregates in poly 3 methyl thiophene, PMeT, together with the analysis of their catalytic properties toward the H^+ reduction into H_2.

II. EXPERIMENTAL

The grafting of the polymer on Au electrode involves the oxidation of the monomer, 3 methyl thiophene 5.10^{-1}M at + 1.35V/SCE in $CH_3CN-N(Bu)_4SO_3CF_3$ 5.10^{-1}M[7]. The thickness of the doped conducting film can be varied from 50Å to several mm by the control of the electrolysis time. The modified electrode is then rinsed, dried and catho dically polarized for the inclusion of metallic aggregates. A first polarization of the film at +0.3V/SCE in $H_2O-AgClO_4$ 10^{-1}M medium leads to the inclusion of Ag aggregates. This Ag modified electrode is then polarized at -0.3V/SCE in $H_2O-K_2PtCl_4$ 5.10^{-2}M which leads to the inclusion of Pt clusters. This Ag -Pt modified electrode has then been immersed in an acidic medium (pH = 0 ; H_2O-HCl) and its electrochemical characteristics (J = f(V) ; J = f(t) at V = -0.4V/SCE) have been determined.

The morphology of this Ag and Pt loaded PMeT has been studied by SEM and TEM techniques (JEOL 120C α and JSM 50A).

III. RESULTS AND DISCUSSION.

The morphology of these Ag and Pt loaded PMeT has been realized on thick polymer deposits.

The SEM picture of (PMeT-Ag-Pt), with 80% Ag and 50% Pt (polymer weight %), clearly shows that the Ag aggregates are mainly located along the polymers fibers (Fig. 1) and the Pt aggregates are deposited on the PMeT surface.

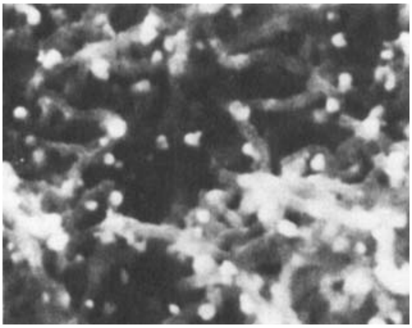

Fig. 1 : SEM picture of Ag aggregates included in PMeT by multistep procedure (X 10 000).

The size and the homogeneity of the distribution of the Ag aggregates in the polymer can be controlled by the electro-chemical procedure used for the inclusion :

- If the Ag aggregates are included in the polymeric matrix in a single electrochemical step, they appear broadly distributed and their sizes lies in the range 300 Å-several µm, big Ag particles being intercalated between the polymer fibers Fig. 2.

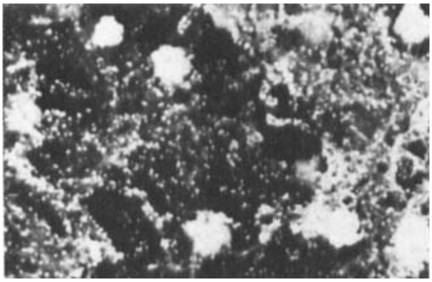

Fig. 2 : SEM picture of Ag aggregates included by a single procedure-large particles of several µm are included between the fibers (x 3000).

- Incontrast, the aggregates are homogeneously localized along the polymer fibers with smaller sizes (20-200Å) if the same amount of Ag is included in the polymer by a slower multistep procedure (Fig. 3).

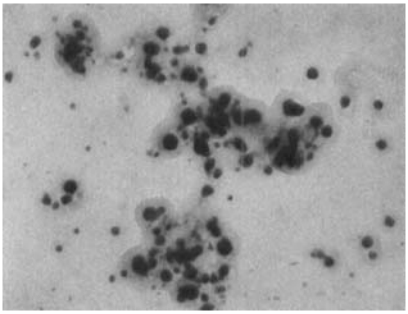

Fig. 3 : TEM pictures of Ag aggregates in PMeT (multistep procedure ; particles size : 20-200Å).

The Pt aggregates more difficult to analyze due to their lower concentration, are essentially located near the polymer surface. These results show that a different role can be attributed to these two metallic aggregates :

- the Pt one, exert a catalytic role at the polymer-electrolyte medium interface,

- on the other hand, Ag may assist the bulk conductivity, the more homogeneously it is distributed along the polymer fibers.

These hypothesis have been confirmed by the study of the electro chemical proton reduction process in acidic medium (pH = 0). Fig. 4

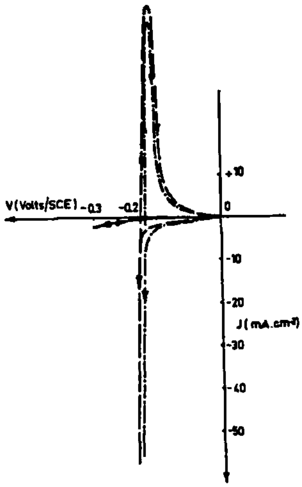

Fig. 4: J-Vcurve obtained in acidic medium (pH = 0, H_2O-HCl) at 50mV/s sweep rate

——— : Au-PMeT (1700Å) or Pt-PMeT (1700Å)

— — : nacked Pt electrode

•—•—•: Au-[PMeT (1700Å)-Ag(80%) - Pt(50%)]

shows the J-V curves for several modified Au electrodes :

- with a nacked Au electrode, the current density remains low in all the cathodic range, 0 to -0.5V/SCE (Fig. 4a); with an Au electrode coated with either undoped PMeT, or Ag loaded PMeT, [PMeT-Ag], J remains in the same low intensity range (Fig. 4b).

- with Pt aggregates in the same [PMeT-Ag] electrode, [PMeT-Ag-Pt], the J-V curve is similar to that obtained on a platinized Au electrode (Fig. 4c). A very sharp increase at -0.2V/SCE, due to the H^+ reduction into H_2 and an anodic peak corresponding to the back reaction when the potential is reversed.

The influence of the Ag and Pt concentrations, and of the film thickness on the J values, when the [Au-PMeT] electrode is polarized at -0.4V/SCE in H_2O-HCl, pH = 0 has been investigated :

- when for a constant Ag concentration in a 1700 Å thick PMeT film, the amount of included Pt is varied, J firstly increases and reaches a plateau : Pt content $\simeq 8.10^{-6}$ g, instead of 3.10^{-6} g for a platinized [Ag-Au] electrode. This difference should correspond to a decrease in the Pt aggregates size.

- Same J variations are observed when different Ag amounts for a constant Pt value are included in the same 1700 Å thick film. This behavior can be interpreted by an enhancement of the conducting properties of PMeT.

- For the optimized Ag concentration (80% polymer weight) and Pt content (50%), the J variations with the thickness of the films is shown in **Fig. 5** : when d < 500 Å, J is lower than that observed

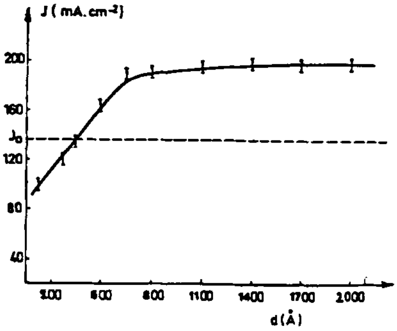

Fig. 5 : Influence of the film thickness d on J.

- - - - - : Au-Pt-Ag electrode

——— : Au-[PMeT-Ag-Pt]

for a [Au-Ag-Pt] electrode and can be due to an inhomogeneous distribution of metallic aggregates. But, when d > 600 Å, J increases and reaches a value of 200mAcm^{-2} : H^{+}reduction yield higher, by more than 50%, than on [Au-Ag-Pt] electrode (130mAcm^{-2}).

The stability of this catalytic system has also been tested and compared to the corresponding one derived from polypyrrole [PP-Ag-Pt] and also to a platinized Ag coated Au electrode [Ag-Pt]. Fig. 6 shows the evolution of J with the polarization time :

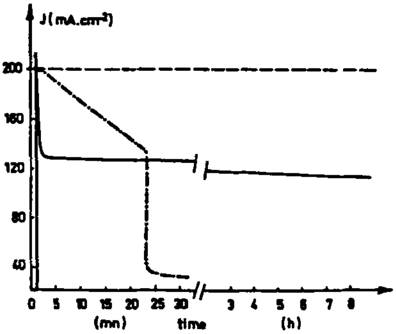

Fig. 6 : Stability of J with time (pH = 0 ; V = -0.4V/SCE)
——— : nacked Pt electrode
– – – : Au-[PMeT-Ag-Pt] electrode
— — : Au-[PP-Ag-Pt] electrode

- With the [Ag-Pt] system, J continuously decreases, due to the migration and aggregation of the Pt clusters on the surface.

- With the [PP -Ag-Pt] system, J rapidly decreases, which is accompanied by a change of the polymer color from brown to yellow. After 25mn, J suddenly falls, due to the peeling of the polymer.

- Incontrast, the [PMeT-Ag-Pt] system is very stable, J remaining constant even after a 170 h cathodic polarization run.

IV CONCLUSION

In conclusion, we have shown that Ag and Pt aggregates can be electrochemically incorporated in an organic conducting polymer like PMeT. The Ag aggregates, which are located along the polymer fibers, assist the electronic conduction in the polymer. The Pt aggregates, mainly located near the surface, show an enhanced catalytic activity. The [PMeT-Ag-Pt] system is able to catalyze the H^+ reduction with current density of 200mAcm^{-2}, which is 50% higher than that observed on [Au-Ag-Pt] electrode.

A remarkable stability with time has been obtained under polarization, which reveals that PMeT is not affected by notive H_2 and that Pt clusters do not migrate and aggregate.

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