ELECTRONIC AND IONIC TRANSPORT PROPERTIES OF ELECTRODEPOSITED POLYPYRROLE FILMS

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Résumé - Des films de polypyrrole ont été déposés par voie électrochimique sur des électrodes d'inox. Les conditions d'obtention du dépôt sont précisées (densité de courant, température).

Le rapport de la conductivité électronique dans le sens parallèle à la surface du film sur la conductivité électronique le long de la surface du film est inférieur à 10^3.

La variation du coefficient de diffusion des ions perchlorates dans le film correspond à une énergie d'activation de 30 kJ/mole.

Abstract - Polypyrrole films have been electrodeposited on stainless steel electrodes. We precise here the limits (current density, temperature) in which a conductive film can be obtained.

The ratio of the electronic conductivity perpendicular to the film surface over the electronic conductivity parallel to the film surface is smaller than 10^3.

The dependance of the perchlorate ions diffusion coefficient versus temperature corresponds to an activation energy of 30 kJ/mole.

ELECTROPOLYMERISATION

The electrochemical synthesis of polypyrrole films has been performed by DALL'OLIO et al in 1968 (1). The medium used was a solution of pyrrole and sulphuric acid in water. The polypyrrole film obtained was in the oxidation state of one positive charge for three to four pyrrole rings. Its conductivity was about $8\ \Omega^{-1}\ cm^{-1}$.

This synthesis was also performed in a non aqueous medium pyrrole, $N\ (Et)_4\ BF_4$ in CH_3CN, by DIAZ et al in 1979 (2). The oxydation state of the film was : one positive charge for four to five pyrrole rings, and the conductivity about $100\ \Omega^{-1}\ cm^{-1}$

We report here experimental results concerning the electrochemical deposition of polypyrrole from a 0.05 M pyrrole, 1 M $LiClO_4$ in propylene carbonate medium.

As shown in fig. 1, the diagram of the product obtained as a function of the current density and the temperature exhibit three different regions corresponding to the following cases.

(i) when the current density is lower than $1\ \mu A/cm^2$, there is no deposition but only a polymerisation of a powder of polypyrrole which falls at the bottom of the cell.

(ii)   when the current density ranges from $1 \mu A/cm^2$ to $10^5 \mu A/cm^2$ and the tempera-
       ture from $-10°C$ to $+80°C$, a conductive polypyrrole film is deposited on
       the electrode.

(iii) when the current density is higher than $10^5 \mu A/cm^2$ or when the temperature
       exeeds $80°C$, an insulating film is deposited on the electrode.
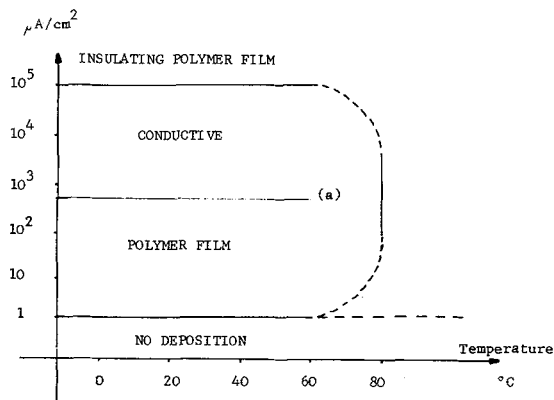
$\mu A/cm^2$

Fig. 1 : limits of polypyrrole film electrodeposition as a function of temperature
         and current density.

Fig. 2 shows the variation of the film conductivity versus temperature when the
polymerisation conditions vary as shown in line (a) of fig. 1 (current density
equal to $50 \mu A/cm^2$, temperature ranging from $-10°C$ to $+50°C$).
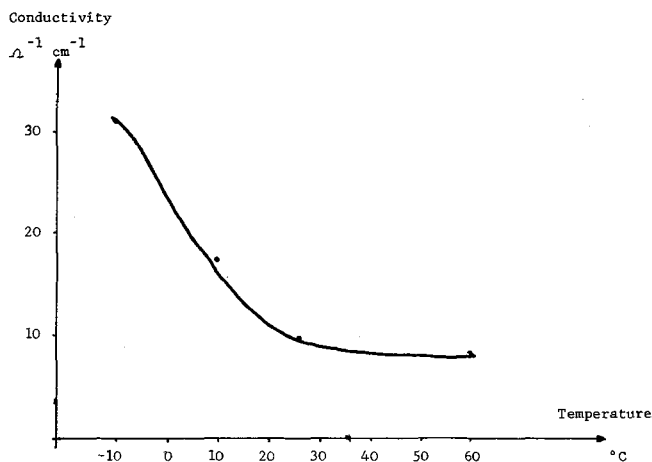
Conductivity

$\Omega^{-1} cm^{-1}$

Fig. 2 : Conductivity of a $30 \mu m$ thich polypyrrole film vs electrodeposition tempe-
         rature.

         Conditions of polymerisation : constant current $50 \mu A/cm^2$
                                         0.05 M C_4H_5N, 1 M $LiClO_4$ in propylene carbo
                                                                            nate

These results are in good agreement with those of PREJZA et al (3). As a matter of fact, these authors, studying a pyrrole, N $(Et)_4$ BF_4 in acetonitrile medium, observed different types of polypyrrole depending on the metal substrate and the current density during electrodeposition.

ELECTRONIC CONDUCTIVITY OF THE FILM :

In order to obtain informations concerning the chain orientations, we attempted to measure the film conductivity in the directions parallel and perpendicular to the film surface.

A conventional two probes method was employed. The resistancy of the film was measured as a function of the distance between two platinum probes. The bulk conductivity of the film and the surface contact resistancy of the probes were derived from the data.

Within the precision of our measurements, no anisotropy of the bulk conductivity was detected on the investigated samples (10 μ m - 1 mm thickness). The anisotropy of the conductivity, defined as the ratio of the conductivity along the film surface over the conductivity through the film is smaller than 10^3.

IONIC DIFFUSION IN THE FILM

We have applied potential steps (-0.6 V, + 0.2 V vs Ag/Ag$^+$ 10^{-2}M) to the polypyrrole électrode in a 1 M $LiClO_4$ in propylene carbonate medium, producing by this way successive reductions and oxidations of the polymer. The current response versus time was a linear function of $t^{-\frac{1}{2}}$. Such a response indicates that the current density is limited by a mechanism similar to the diffusion in a semi infinite medium. The diffusion coefficient was calculated in the usual way (4). Its typical value was 5×10^{-12} cm^2/s at 25°C. Plot of the diffusion coefficient versus temperature in Arrhenius coordinates indicated an activation energy of about 30 kJ/mole.

Fig. 3 et Fig. 4 show the variation of the perchlorate ions diffusion coefficient as a function of the temperature for the reduction of oxidized polypyrrole and for the oxidation of reduced polypyrrole respectively.
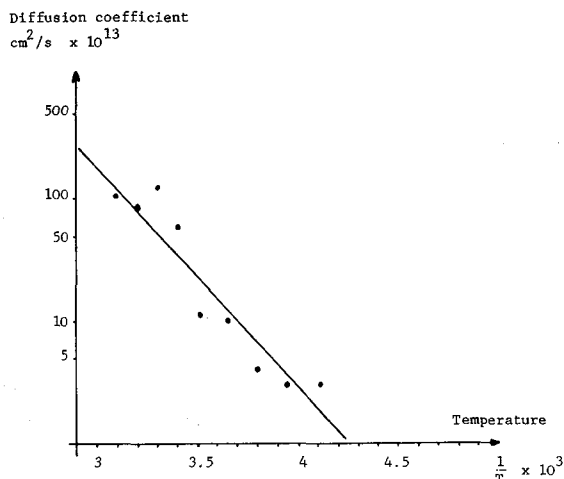

Diffusion coefficient
cm^2/s x 10^{13}

Fig. 3

Diffusion coefficient of the perchlorate ions as a function of temperature for the reduction of oxidized polypyrrole film.

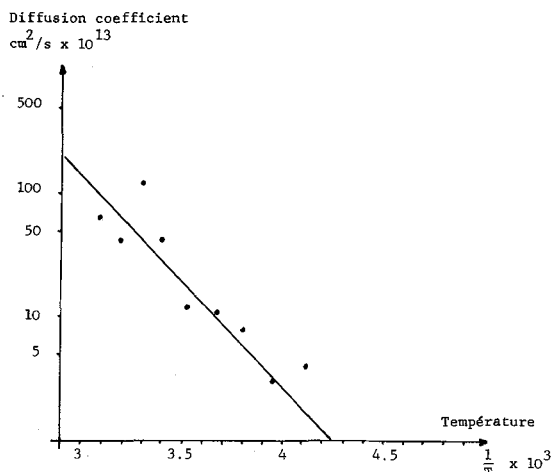Medium : 1 M $LiClO_4$ in propylene carbonate

Fig. 4

Diffusion coefficient of the perchlo-
rate ions as a function of temperature
for the oxidation of reduced polypyr-
role film.

Medium : 1 M LiClO$_4$ in propylene car-
bonate.

These values can be compared to these obtained for the H$^+$ diffusion in γ MnO$_2$:
94 kJ/mole and 2.5 x 10^{-10} cm^2/s at 50°C.

From this comparison, we can conclude that the kinetic properties of polypyrrole
are less temperature dependant than those of γ MnO$_2$.

CONCLUSION

The polypyrroles appaear to be very promissing electrode materials, due to their
important bulk conductivity, their fast ionic diffusion, and to the small tempera-
ture dependance of the ionic diffusion coefficient.

Because of the different properties of the polypyrroles obtained, depending on the
experimental conditions, a better characterisation of the polypyrrole, and a better
understanding of the electropolymerisation processes are necessary.

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