# Electrodeposition of metals and magnetic alloys onto conducting polymeric substrates

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# **RÉSUMÉ:**

En préparant un composite conducteur polycarbonate/noir de carbone, nous avons obtenu un nouveau matériau susceptible d'être utilisé comme cathode pour la préparation électrolytique de recouvrements métalliques. Ces cathodes sont comparées à des cathodes de Ppy déposé sur polycarbonate. Nous décrivons ici la réalisation d'alliages magnétiques en couches minces. Ces alliages Lanthanides/Métaux de transition sont préparés en milieu organique (Formamide:FA) où les cathodes constituées de films minces de polypyrrole conducteur ne sont plus utilisables. Le caractère métallique et amorphe de ces alliages est démontré par analyse RBS.

Mots clés: Polymère conducteur, dépôts électrochimiques, alliage magnétique.

#### ABSTRACT:

A new composite material prepared by mixing polycarbonate with carbon black has been tested as new kind of cathode. This material has been compared with a conducting polymer precipitated onto polycarbonate, both in aqueous and organic solutions. We report some examples of electrodeposition of magnetic alloys (Lanthanides/Transition metals) in Formamide. In this medium, the use of thin polypyrrole films cathodes had remained impossible. The preparation of amorphous and magnetic alloys onto PC/carbon black is evidenced by RBS.

Key words: Conducting polymer, electrodeposition, magnetic alloy.

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### INTRODUCTION:

The electrodeposition of rare earth alloys with transition metals in thin layers has appeared as an alternative path for the preparation of magnetic films for novel functions such as magnetic or photo-magnetic memories [1]. In this process, the cathodes consist of Cu, Au or ITO glass which are diamagnetic materials. In this paper, we intend to investigate the behaviour of several organic composites when used as cathode. Thus we prepared films of polypyrrole (PPy) supported by polycarbonate foils (PC) and also foils of conductive composites molded from a mixture of carbon black (15%) (XE-2 Degussa) and polycarbonate (PC) (Macrolon 3103 Bayer). PPy cathodes have been used in water for the electrodeposition of metals and alloys [2],[3] while plating of conducting composites seems unknown.

### **EXPERIMENTAL:**

The Ppy films were precipitated at room temperature onto the PC foils from an aqueous solution containing: Py 2.10<sup>-2</sup> M; FeCl<sub>3</sub> 10<sup>-1</sup> M; FeCl<sub>2</sub> 10<sup>-2</sup> M; Doping agent 10<sup>-2</sup> M: PTS<sup>-</sup> (Paratoluenesulfonic acid sodium salt). A black, thick and homogeneous PPy film is obtained after 2 hours. The composite material is prepared by mixing carbon black with PC (260°C) and then pressed at 25 Kg/cm<sup>2</sup>; in these conditions regular plates, 1 mm thick, are obtained. We have checked the capability to use both types of material as cathodes by Cu and Co plating in aqueous solutions. Regular deposits were obtained with the PPy films only by a progressive immersion of the cathode in the electrochemical bath while the cathodes of the composites were homogeneously plated by direct immersion.

We report here results obtained from electrochemical baths containing lanthanide chlorides (LnCl<sub>3</sub>) (DyCl<sub>3</sub>, GdCl<sub>3</sub>, TbCl<sub>3</sub>, SmCl<sub>3</sub>) and transition metals chlorides (TMCl<sub>2</sub>) (FeCl<sub>2</sub>, CoCl<sub>2</sub>) with LnCl<sub>3</sub>/LnCl<sub>3</sub> + TMCl<sub>2</sub> = 35 or 80% without conducting salt in dry FA. The total concentration was fixed at 0.1M. We worked in galvanostatic conditions with a pulsed current (ON: 0.1s; OFF: 1s) and current densities ranging from 5 to 50 mAcm<sup>-2</sup>.

#### **RESULTS:**

We found that the PPy films were unadapted to the organic medium: it remained impossible to regularly plate the cathodes even with progressive dipping in the solution. The deposition proceeded only in some areas while the remaining part of the cathode became yellow. The PPy film was electrochemically reduced and it became an insulator. This observation was readily confirmed by X-Rays fluorescence analysis: the dopant has dissapeared since sulfur is no longer evidenced. In aqueous solutions, the electrochemical reduction rate of the dissolved ions is greater than the reduction of the polymer itself and that difference of kinetics is in favour of regular plating. Encouraging results were attained with the PC composite where regular layers of alloys were noticed. We report some characteristics of the alloys prepared on PC composites based cathodes. The Rutherford Back Scattering (RBS) technique clearly demonstrates the presence of Gd and Co in thin layer while C and O from the PC based composite give rise to the energy bands expected from the principles of the RBS analysis. Metal chlorides are not precipitated during the electrolytic process since no peak corresponding to Cl (E= 1.59Mev in our experimental conditions) is observed. Our alloys are not oxidized since we do not observe the presence of superficial oxygen which would give rise, in RBS spectra, to an additional peak at E=0.85 Mev superposed to the inflexion point of the energy profile corresponding to oxygen of the PC. In this example the ratio Gd/Co equals 1/50.

The alloys are amorphous and exhibit magnetic properties. These properties are now investigated by magnetometric measurement.

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