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The use of conducting polymers as cathodes for the electrochemical deposition of magnetic transition metal/rare earth alloys

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We report the electrodeposition of Cu and Ni in aqueous solutions together with the deposition of lanthanides (Gd, Sm, Dy, Tb) and amorphous magnetic alloys of lanthanides with transition metals (Fe, Co) onto various polymer cathodes in formamide solutions. We used conducting polymers (polypyrrole, PPy; polyethylenedioxythiophene, PEDOT) sprayed on different substrates and in addition composite materials based on carbon black (CB) mixed either with polyethylene (PE) or with polycarbonate (PC). In the latter case, the conducting material is easily shaped out in various forms. When deposited on some of these substrates, the alloys appear as an interesting material for magneto-optic recording. The electrochemical process was used for the preparation of Gd/Co and Dy/Fe alloys for which the measured coercitive fields ranged from 250–300 Oe (Dy/Fe) to about 350 Oe (Gd/Fe). We demonstrated also the feasibility of an additional electrografting of a transparent protective layer of polyacrylonitrile (PAN) in order to avoid the corrosion of the alloys by the atmosphere.

Introduction

The electrochemical deposition of various metals involved in technological applications, such as Ti, Zr, Al, lanthanides and actinides, is only feasible in molten salts or in organic solvents at room temperature because of their extended electroactivity range. Numerous organic solvents were found to be convenient for these applications[1] but it appears that formamide (FA) is the best medium for the electrodeposition of most rare earth metals (RE) and for the preparation of magnetic RE–transition metal (TM) alloys.[2,3] When the target path is the preparation of these alloys as thin layers (1–5 μm), it is necessary to use cathodes which are inert with respect to the solvent and whose magnetic properties will not affect those of the deposited layers.

Until now, Au, Cu, and ITO glass cathodes[2,3] were commonly involved but, in the case of FA, it appeared to us that Cu metal partially reduced the solvent or reacted with the solvent by an undefined mechanism. Whatever the corrosion process, Cu^{2+} ions were present in the electrochemical bath and were deposited in turn into the alloys. ITO glass is claimed to give good results[4] but we have reported many cases of irregular deposition. Moreover, this substrate exhibits some brittleness.

Thus we looked for new cathodes that are built from organic materials. Two different approaches have been investigated here. First, we paid attention to conducting polymers such as polypyrrole (PPy)[5] and polyethylenedioxythiophene (PEDOT).[6] In this approach, an insulating substrate, such as a polycarbonate plate, is made conducting by chemical precipitation of a conjugated conducting polymer (PPy or PEDOT) as a thin layer onto the surface of the transparent polycarbonate. As described in the literature,[7] conducting polymers are widely used in microelectronics, that kind of conducting polymer being used as intermediate layers in lithographic patterning.[8] This would thus open the door to the manufacture of small magnetic entities by electrochemical growth of a magnetic alloy on such patterned substrates, leading, for instance, to new magnetic recording media. It should also be mentioned that PEDOT exhibits some transparency when it is deposited as a thin layer onto the substrate,[9] this transparency being a requirement for magneto-optic applications.[10] However, in this approach, we have to consider that these conducting polymers are electroactive and that they are insulating in their reduced state.[11] The cathodic deposition of a magnetic alloy on the surface thus remains a real challenge by this technique.

In a second path, polymer based composite materials[12–14] such as hot pressed mixtures of polyethylene/carbon black (PE/CB) or polycarbonate/carbon black (PC/CB), containing enough carbon—*i.e.* 15 wt%—to secure good conductivity have been investigated. These bulk materials are easily processed into various shapes and are mechanically quite resistant like metals, and moreover constitute lighter and cheaper substrates.

In this paper, we report results obtained for the deposition of RE/TM alloys onto the above mentioned polymeric cathodes. As these alloys are very reactive to oxygen and moisture, we also briefly describe an additional electrochemical process to preserve the alloy using a transparent thin layer of grafted polyacrylonitrile (PAN).[15] The so prepared material ought to be eligible for magneto-optical applications.

Experimental

Electrode preparation

1 PPy based electrodes. *1.1 Electrochemical deposition onto a conducting substrate (PPy/Pt).* In a first stage of the work, Pt anodes were used in aqueous solutions containing $LiClO_4$ or polystyrene sulfonate as conducting salts (0.1 M) for the oxidation ($E = +0.7$ V *vs.* SCE) of the monomer (Py: 0.1 M) in order to deposit adherent films of PPy onto the metal, the thickness of the film being controlled by the electrolysis time (1 C cm^{-2} leading to 4 μm thick films).[16]

1.2 Chemical deposition onto an insulating substrate (PPy/PC). PPy conducting films were prepared in routine by slow precipitation (2 hours) of the polymer onto transparent foils

(10 × 20 mm, thickness 1 or 2 mm) of commercially available PC from a solution consisting of pyrrole (0.022 M), $FeCl_3$ (0.102 M), $FeCl_2$ (0.01 M) and 1,5-naphthalenedisulfonic acid sodium salt (NDSA, 0.01 M) as doping agent. These experimental conditions were adapted from literature data.[17,18] The polymeric layers adhere fairly well to the PC substrate and they were rinsed in distilled water and dried at 100 °C for 2–3 hours. The black conductive layers are stable in air and ready to be used as cathodes in FA. One edge of these electrodes was covered with a thin strip of silver paint to secure good electric contact with the cathode holder (alligator clip).

The PPy structure is evidenced by IR spectroscopy by comparison with data previously published by Oddi *et al.*[19]

2 PEDOT based electrodes. *2.1 Electrochemical deposition onto a conducting substrate (PEDOT/C).* The electrochemical deposition of PEDOT on vitreous carbon anodes (C) (plates 20 × 10 mm) was carried out in acetonitrile (ACN) solution containing 5×10^{-2} M EDOT and 5×10^{-2} M Et_4NClO_4 as a conducting salt. The polymerisation was achieved at constant potential ($E = +1.5$ V *vs.* a Pt foil acting as a pseudoreference electrode). The current amount was set up at 500 mC cm^{-2}. Under these conditions, the thickness of the PEDOT films was about 2.6 µm.[20]

2.2 Chemical deposition onto an insulating substrate (PEDOT/PC). The chemical synthesis of PEDOT must be performed in an organic medium (ACN) and in this case, the precipitation of the polymer onto PC plates was impeded by the slow dissolution of PC in the solvent. Thus PEDOT was prepared separately from an ACN solution (EDOT 0.1 M, $FeCl_3$ 0.2 M, 50 °C, reaction time 4 hours) according to a procedure described by Heywang and Jonas.[21] The solution was cooled and sprayed onto the PC foils until the support was completely covered. The electrodes were thoroughly rinsed with ACN and water to remove the excess of monomer and to eliminate $FeCl_3$. SEM investigations demonstrated the formation of regular layers of PEDOT (Fig. 1A) and showed that despite intense washing of the material, PEDOT still covers homogeneously the PC, revealing its good adherence to the substrate.

3 Carbon black composites (PE/CB and PC/CB). The composites containing 15 wt% carbon black (Ketjenblack EC 600 JB) were prepared by mixing with the appropriate polymer in a Brabender mixer at 25 rpm and at 65 rpm after the polymer melting. The temperature was about 250 °C for PC and 180 °C for PE (external heating); the composites were prepared within 10 minutes. We used Makrolon 3101 (Bayer, polycarbonate sheet (PC)) and Exceed 109 (Exxon, polyethylene sheet (PE)). The resulting material was either extruded (bar diameter: 3 mm) or hot-pressed as thin plates, 2 or 3 mm thick.

Chemicals

Anhydrous $FeCl_2$, $FeCl_3$, $CoCl_2$, $GdCl_3$, $DyCl_3$, $TbCl_3$ (Fluka or Cerac) were used as received. Tetraethylammonium perchlorate (Et_4NClO_4; Aldrich) was dried for 24 hours under reduced pressure at 60 °C. Ethylenediamine (EDA) was dried over molecular sieves. Naphthalenedisulfonic acid sodium salt was used as received.

FA 99.5% (Janssen Chimica) was dried over 3 Å molecular sieves for three days and then distilled under dynamic vacuum. Voltammetric and differential pulse polarography analyses indicated the absence of residual water. Acetonitrile and acrylonitrile were dried over CaH_2 for three days and distilled under vacuum.

EDOT (Bayer) and Py (Aldrich) monomers were distilled under dynamic vacuum before use.

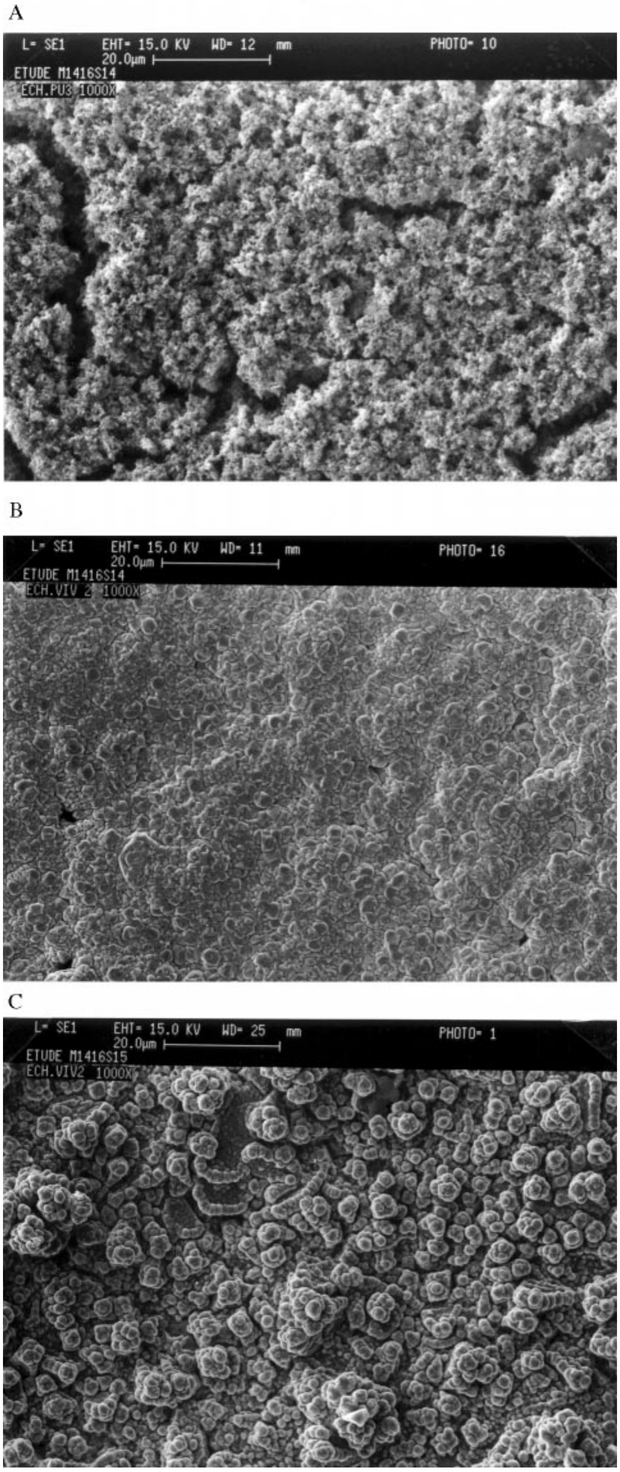

Fig. 1 Micrographs (mag. 1000 ×) showing the microstructures of (A) PEDOT chemically synthesised and sprayed onto a PC plate, (B) Cu thin layer deposited on PEDOT/PC, and (C) Gd/Co alloy deposited on Cu/PEDOT/PC.

Electrochemical plating baths

Copper and nickel plating baths corresponded to the usual compositions. $CuSO_4 \cdot 2H_2O$: 60 g l^{-1}; H_2SO_4: 60 g l^{-1}; C_2H_5OH: 50 g l^{-1} and $NiSO_4 \cdot 6H_2O$: 300 g l^{-1}; $NiCl_2 \cdot 6H_2O$: 60 g l^{-1}; H_3BO_3: 45 g l^{-1}.

Equipment

For voltammetry and related techniques, we used a classical three electrode cell and a Pt pseudoreference electrode as previously described.[22]

The metals and alloys were deposited in a cell consisting of one cathodic central compartment and two lateral anodic compartments in order to secure homogeneous current lines on the cathode area; the total area of the two anodes was equal to 20 cm^2 *vs.* 2 cm^2 for the working electrodes. Most of the work was carried out with soluble anodes (either Co or Fe foil). All the preparations in FA were carried out in a glove box under N_2 atmosphere. Constant current, either continuous or pulsed, was supplied by a Tacussel PRT 200/1 potentiostat/galvanostat while PAR/EGG equipment (270/1) was used for transient techniques.

The Rutherford backscattering technique (RBS) was used to characterise the alloys composition and homogeneity. A beam of 2.5 MeV α particles was produced by a Van de Graaf accelerator. The backscattered particles were detected with an annular PIPS detector (active area = 100 mm^2 and resolution = 19 keV). The α particles were detected in a solid angle of 0.007 sr.[23]

A scanning electron microscope (Cambridge Leica) coupled with an EDAX analyser (Explorer) was used to analyse the morphology of the electrodeposited alloys and their composition.

Magnetic measurements were carried out at room temperature by using a vibrating sample magnetometer, the magnetic field varying from -1.5 to 1.5 T.

After dissolution of the alloy with HNO_3, inductively coupled plasma (ICP) analysis was used to determine the metal composition.

Results and discussion

1 Cathodic characteristics

1.1 PPy/PC and PEDOT/PC electrodes. The capacity of PPy and PEDOT composites to be used as cathodes was examined in aqueous solution with Cu and Ni plating electrochemical baths. As mentioned in the literature,[18] Cu is very rapidly electrodeposited from this medium, and Cu metallic coating over PPy should be easily obtained.

With PPy thin films precipitated onto PC plates, an appropriate Cu plating was obtained by progressive immersion of the plate—cathodic potential applied—into the bath as described by Genies.[5] If total immersion was immediately achieved, copper plates only at the air–solution interface; this observation is a matter of controversy with previously published data.[17] Similar behaviour was noticed with PEDOT, *i.e.* deposition at the interface only but, in that case, a somewhat different plating process has to be considered. To prevent the detachment of Cu, the entire electrode was immersed into the bath and withdrawn step by step to produce a regular plating. The morphology of the electrodeposited Cu is shown in Fig. 1B. On both PPy and PEDOT cathodes, Ni plating was heterogeneous and it was necessary to use a preliminary Cu deposition. Fig. 2A shows the structure of the Ni electrochemically deposited onto the Cu/PEDOT/PC electrode. These results probably correspond to the difference between the standard potentials of the Cu^{2+}/Cu and Ni^{2+}/Ni couples compared to the polymer critical potential of reduction.

1.2 PE/CB and PC/CB electrodes. As far as the composite electrodes are concerned, complete plating (Cu or Ni) is achieved by direct immersion of the whole cathode in the plating bath. The ohmic drop is low and the applied potential between anode and cathode is lowered to 5 V corresponding to a mean current density of 30 mA cm^{-2}, instead of 30 V with PPy cathodes. It is important to note that these CB composites are electrochemically inert and thus the electroactivity window is only limited by solvent reduction, while in the case of PPy and PEDOT polymers this window also depends on the electroactivity of the polymer in the studied medium; therefore with these last electrodes, we have to check their electrochemical behaviour in the solvent required for the alloy synthesis, *i.e.* in FA.

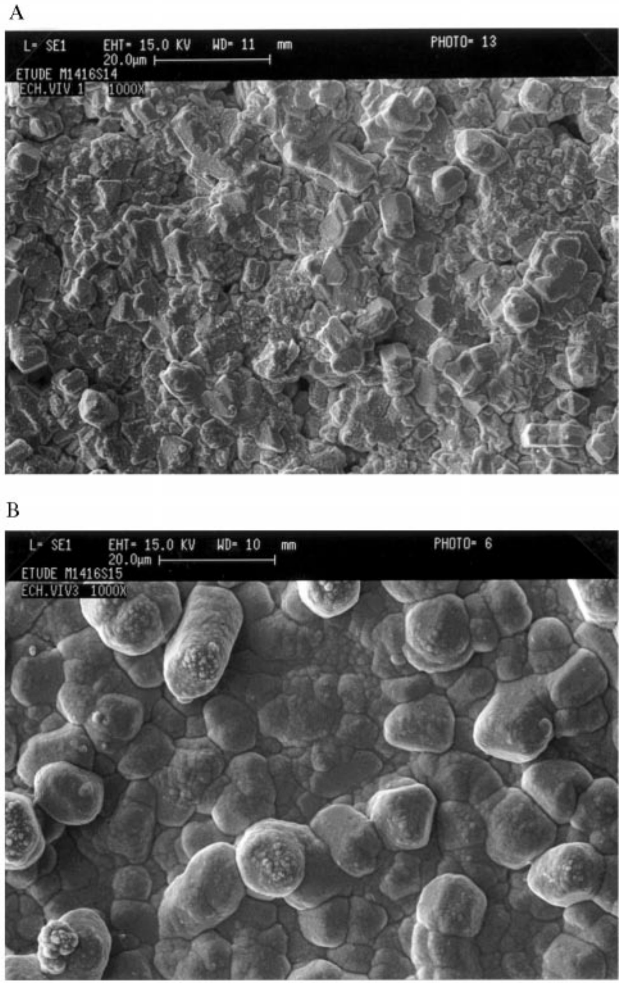

Fig. 2 Micrographs (mag. 1000×) showing the microstructures of (A) Ni coating on Cu/PEDOT/PC, and (B) Gd/Co alloy on Ni/Cu/PEDOT/PC.

1.3 Electroactivity in FA. The electroactivity of PPy and PEDOT deposited onto Pt was characterised in the organic medium (FA, Et_4NClO_4 0.1 M) by cyclic voltammetry. With a scan rate of 25 mV s^{-1}, the potential peak for the reduction of PPy appears at -0.2 V *vs.* Pt, *i.e.* probably at a less cathodic value in this solvent than in water, and PPy becomes an insulating material when the potential exceeds -0.5 V *vs.* Pt as demonstrated by the drop of the current to the residual value. In contrast, PEDOT is reduced at a more cathodic potential peak, -0.7 V, than PPy at the same scan rate in FA.

In addition, with a scan rate of 100 mV s^{-1}, we observed that at a more cathodic potential, -1.2 V *vs.* Pt, the conductivity of PEDOT is still retained since the current still comes up to 7 mA cm^{-2}. The latter potential is in good agreement with the alloy deposition.

2 Alloys deposition onto conducting polymer thin layers

2.1 Onto PPy cathodes. On PPy/Pt (electrochemical synthesis) when the film thickness is lower than 1 µm, the Gd/Co alloy is formed on the underlying Pt electrode through the PPy coating, leading to irregular alloy coating of the polymer whatever the counter-ion used for the PPy synthesis. When the film thickness is increased, no alloy deposition occurs, but only the reduction of the PPy film occurs.

On PPy/PC material (chemical synthesis), various attempts to plate Co in FA ($CoCl_2$ 0.1 M) failed: only very irregular deposits were observed and sometimes in the presence of precipitated $CoCl_2$ and of scattered yellow areas corresponding to the reduced (insulating) structure of PPy. We concluded that these PPy cathodes are rapidly reduced in FA and are not suitable for the direct deposition of transition metals in this medium.

2.2 Onto PEDOT cathodes. On PEDOT/C cathodes, homogeneous deposition of Co metal was achieved in pulsed galvanostatic electrolyses with an ON/OFF ratio equal to 0.1/1 s from a 0.1 M $CoCl_2$ solution in FA, with current densities from 2.5 to 10 mA cm^{-2} ($Q = 20$ C). Pulsed electrolysis gave much better results than continuous electrolysis. This technique and the influence of the electrolysis time (ON) and rest time (OFF) have been previously reported in preliminary experiments with Cu and Au cathodes.[4] With conducting polymers, during the OFF time, the diffusion layer is indeed reloaded with Co^{2+} ions and also the partially reduced PEDOT is reoxidized. SEM/EDAX analysis confirms the good coating of the polymer by the metal; the absence of Cl in the EDAX spectrum is evidence of the formation of metallic Co which is not contaminated by the precipitation of the chloride salt. The feasibility of regular deposition of metallic Co on these cathodes has therefore been proven.

Gd/Co alloys were prepared from $GdCl_3/CoCl_2$ solutions (Gd/Co = 1, $[GdCl_3]+[CoCl_2] = 0.2$ M) at 5 and 10 mA cm^{-2} ($Q = 25$ C), since a lower current density (2.5 mA cm^{-2}) leads to poor coating of the surface. The structure of the deposited layer is shown in Fig. 3. EDAX and RBS analyses (Fig. 4) show that the Gd content is increased from 1.5 to 4 at% when the current density is increased from 5 to 10 mA cm^{-2}. The absence of Cl is also confirmed by these measurements. It must be noted that compositional analysis of a Gd/Co alloy deposited under the same conditions onto a Cu foil only gave a Gd content lower than 1 at%.

PEDOT appears thus to be more stable than PPy and allows the deposition of the alloy onto its surface.

On PEDOT/PC electrodes, the direct deposition of the alloy is more difficult. Indeed, we think that, when the conducting substrate (glassy carbon) is replaced with insulating polycarbonate, the PEDOT has to insure both the electron exchange with the Co^{2+} and Gd^{3+} ions and the electric conductivity in the system. Since this material is less conductive than glassy carbon, an overpotential is required to compensate the ohmic resistance of the system and this probably leads to a quicker reduction of PEDOT, impeding the alloy deposition. To obtain reliable results, we found it necessary to carry out a preliminary deposition of Cu before deposition of the Gd/Co alloys. In this case, under the experimental conditions described above, a maximum Gd content of 3.8 at% was reached. These results can be seen in Fig. 1C, which shows the structure of the so-prepared alloy. We can see a more granular structure for the alloy prepared on this Cu/PEDOT/PC electrode compared to the alloy directly deposited onto PEDOT (Fig. 3). In order to understand the effect of the substrate on the Gd/Co structure, the alloy was deposited after previously coating the Cu/PEDOT/PC with Ni (Fig. 2B). We can see that the specificity of the underlying metal deeply affects the morphology of the Gd/Co alloy (Fig. 1C and 2B) and that the polymer does not directly control the alloy microstructure.

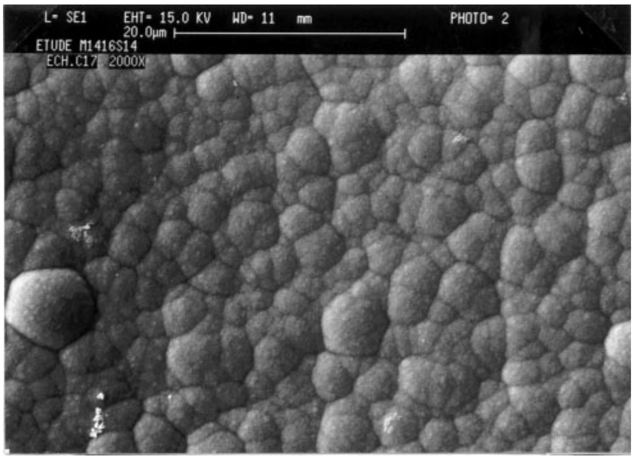

Fig. 3 Micrograph (magnification: 2000×) of the Gd/Co alloy electrodeposited onto PEDOT/C.

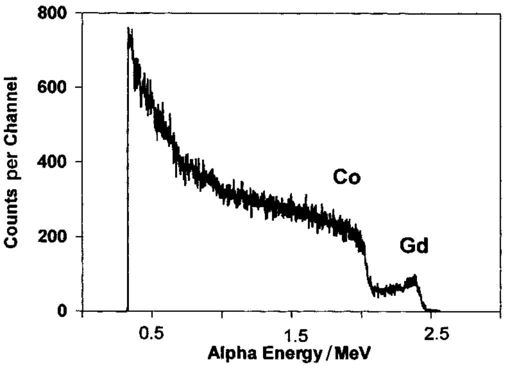

Fig. 4 RBS spectrum of the Gd/Co alloy electrodeposited onto PEDOT/C.

3 Alloy deposition onto carbon black composite materials

3.1 PE/CB. From voltammetric measurements at different scan rates, the reduction of both Co^{2+} (Fig. 5) and Gd^{3+} (Fig. 6) was investigated. The waves are ill shaped, and in each case the wave on the reverse scan crosses the direct scan indicating the deposition of the metals by a nucleation process. In both cases, the anodic stripping peak clearly appears. In the case of Co, an increased current is observed on the reverse scan ($E = -1.2$ V) indicating the easier deposition of Co on the first deposited metal layers compared with its deposition on PE/CB.

Metallic Co was prepared with constant current densities of 25 and 50 mA cm^{-2}. Pulsed electrolyses, without agitation, were involved with an "ON time" fixed at 0.1 s while the "OFF time" was either 1 or 2 s. Under these experimental conditions, homogeneous and pure Co deposits were easily obtained. For shorter "OFF times" (0.2 or 0.4 s) contamination with Cl was detected by X-ray fluorescence analysis.

Gd metal was plated with the same current densities and the same "ON time" but, very surprisingly, complete absence of

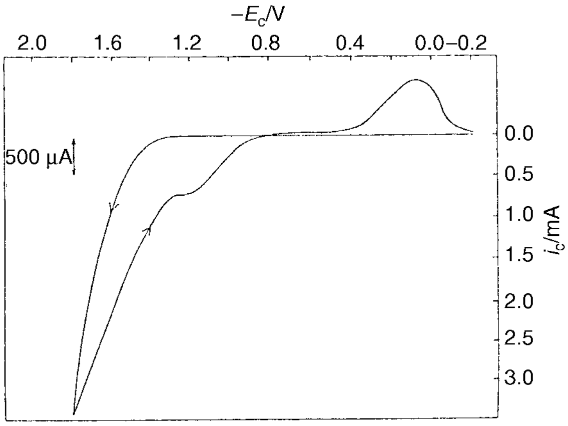

Fig. 5 Cyclic voltammetry recorded on a PE/CB electrode dipped in a $CoCl_2$ (0.1 M) solution in FA.

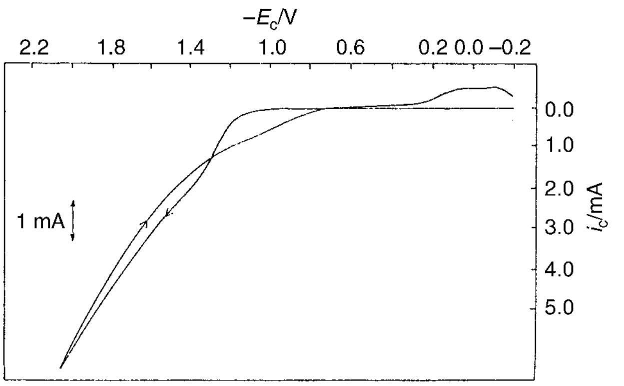

Fig. 6 Cyclic voltammetry recorded on a PE/CB electrode dipped in a $GdCl_3$ (0.1 M) solution in FA.

chlorine in the deposit was only observed for the shorter "OFF time", *i.e.* 0.2 s, according to X-ray fluorescence results. The quantities of deposited Gd metal in each run were determined by ICP analyses: the current yield was found to be equal to 73% for 50 mA cm^{-2} (current quantity 22 C) but only 10% at 25 mA cm^{-2}. In contrast with what usually happens for alloys deposition onto metallic substrates (Cu, Au), it appears that high yields are obtained for high current densities when a polymeric substrate is used.[4] This may be explained by the difference in the ohmic resistance of the two systems, a higher resistance for the polymer requiring a higher current density to optimise the alloy deposition while, in the case of the metal substrate, a too high current density can favour the competing reduction of the solvent and the limitation of the alloy deposition yield.

The Gd/Co alloys were prepared according to some preliminary experiments while taking into consideration data published by Usuzaka and Yamaguchi.[24] The total concentration of $GdCl_3 + CoCl_2$ was fixed at 0.1 M but two different Gd/Co ratios were used: 4/1 and 9/1. Ethylenediamine (EDA, 0.03 M) was added in some experiments in order to complex Co^{2+} and so to shift the Co^{2+}/Co deposition potential towards more cathodic values.[15] Alloys without the presence of chlorine were produced with the two above-mentioned Gd/Co ratios in solution as well, with or without addition of EDA. It seems that EDA has no effect on the alloy composition. The most suitable current densities are between 12.5 and 50 mA cm^{-2} and the current quantities between 15 and 50 C. For instance, we found that with a 50 mA cm^{-2} current, the Gd/Co ratio equalled 9.4 (30 C involved) but was lowered to 2.7 (43 C involved) when the ON/OFF ratio of the pulsed current was changed from 0.1/0.4 s in the first case to 0.1/0.2 s in the second case. In these experiments, the Gd/Co ratio in solution equalled 9/1 and no EDA was added. The maximum Gd content of the alloys reached 74 at% under the following conditions: $i = 50$ mA cm^{-2}; $Q = 22$ C; ON/OFF = 0.2/0.4 s; no EDA added.

In all the so-produced alloys, numerous cracks were distinguished and it appeared that the appearance of these cracks was probably related to the Gd concentration in the alloys, since the alloy Gd/Co (74 at% Gd) is completely splintered (Fig. 7A).

It was found from all these investigations that the composite PE/CB may be considered as an interesting cathode in aqueous solution and in FA for the deposition of transition metals, Gd metal and most likely of other lanthanides. The deposition of transition metal/lanthanide alloys is also feasible, but in this case the presence of fissures will increase the magnetic losses when a high quality magnetic material is required. Finally, we tentatively consider that the inert polymer (PE) impeded the overall adhesion of the alloys and we chose to change PE to another polymer of highly polar character: polycarbonate (PC).

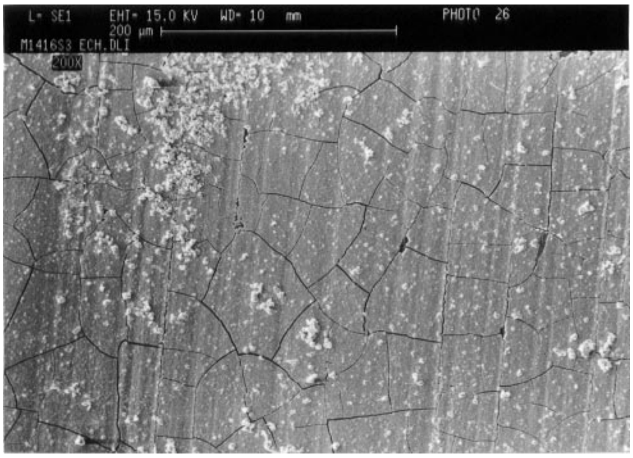

Fig. 7 Micrograph (magnification: 200 ×) of the Gd/Co alloy deposited onto a PE/CB cathode.

3.2 PC/CB. Regular depositions of Gd and Sm metals were carried out from FA solutions ($GdCl_3$, $SmCl_3$ 0.1 M) at 20 mA cm^{-3} and an ON/OFF ratio = 0.2/2.0 s with $20 \leqslant Q \leqslant 40$ C. For greater current quantities, the deposited layers were weakly adherent to the electrode. Moreover, it has to be noted that ageing of these polycarbonate electrodes and a too long stay in the FA solvent led to the polymer swelling and induced electrode cracks. Electrolysis time must therefore be short to alleviate this problem, which did not occur with less soluble PE.

The capacity of this second composite to provide a suitable basis for Gd/Co alloys was checked using the experimental conditions described above. Regular layers were obtained but the amount of Gd in the alloys was only about 1–2 at%. The alloy composition appears to be independent of the current density (25, 50 mA cm^{-2}) and of the presence of EDA. By using bars (diameter: 3 mm) of the extruded material instead of planar electrodes, we recovered samples specially designed for the measurement of a particular magnetic property: the coercive field. With a vibrating sample magnetometer we recorded only weak coercive fields—from 20 to 70 Oe—as determined from the hysteresis loop at room temperature (Fig. 8). However, coercive fields appeared to be more important when the alloys were prepared in the presence of EDA. EDA therefore plays the role of a surface agent leading to alloys of better homogeneity.

Since the PC/CB bulk material can be easily obtained as bars with a shape well suited for magnetic measurements, we have investigated a wider variety of alloys on this substrate.

For comparison, some Sm/Co alloys were prepared from FA solutions containing 0.1 M of dissolved species with [$SmCl_3$]/

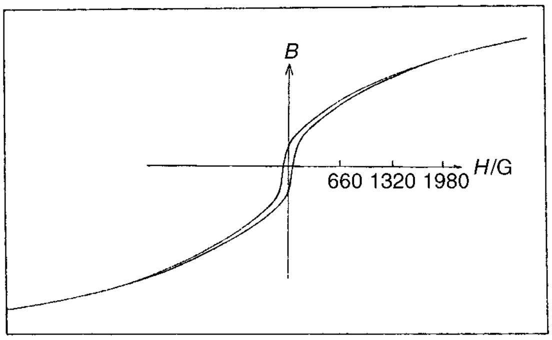

Fig. 8 Hysteresis curve of the Gd/Co alloy deposited onto a PC/CB cathode.

$[CoCl_2] = 9$. Here again the addition of EDA had no meaningful effect on the composition but led to more important coercive fields. The most reliable and reproducible results corresponded to low current densities, 2 and 5 mA cm^{-2}, for which 1 at% of Sm was incorporated in the alloy: the coercive fields equalled 150–160 Oe ($Q = 20$ C; ON/OFF = 0.1/1 s). With a higher current density, 10 mA cm^{-2}, ($Q = 20$ C), the coercive fields dropped to 40–70 Oe and for 50–80 mA cm^{-2}, lower values of the coercive field were noticed (34–40 Oe). In all these cases, metallic alloys were prepared for RBS analyses which indicated the presence of both constituents of the alloy together with the elements characteristic of the underlying polymer (C, O). Moreover, examination of the O peak indicated a contamination of the alloy by O. Indeed, the RBS signal of O shows a high peak at high energy corresponding to superficial O (metal oxide), which overlays the continuous band at lower energy corresponding to the O from the polymer (Fig. 9). This emphasises the necessity to protect the alloy from the atmospheric corrosion.

The preparation of three iron alloys, Tb/Fe, Dy/Fe and Gd/Fe, was also investigated in turn in various experimental conditions. For the system Tb/Fe, between 20 and 50 mA cm^{-2} ($Q = 20$ C), the coercive fields reached values of 100–160 Oe, while irregular values—from 70 to 160 Oe—were the rule for 10 mA cm^{-2}. Here again, the Tb concentration in the alloys reached about 1 at% with a Tb/Fe ratio = 9 in the electrochemical bath.

Dy/Fe alloys were more easily prepared—3-4 at% Dy—with current densities of 30 and 40 mA cm^{-2}, with the coercive field reaching 160–200 Oe and corresponding to regular deposited layers. At 50 mA cm^{-2}, the coercive fields were again higher, 250–300 Oe (ON/OFF = 0.2/2 s; Dy/Fe = 4 in the bath). As far as Fe alloys are concerned, the best results were obtained for the Gd/Fe alloy (Gd 8 at% in the alloy) at 30 mA cm^{-2} and with coercive fields of (350 ± 35) Oe.

4 Grafting of a polymer coating on the alloys

As mentioned above in the introduction, we coated some Gd/Co alloys with PAN from acrylonitrile (AN, 0.1 M) solutions containing 0.05 M Et_4NClO_4 as a conducting salt. This process has been thoroughly discussed in our preceding papers and patents.[25–27] In a classical three electrode cell, the Gd/Co layer was used as a cathode while the counter electrode and the pseudoreference electrode were large Pt foils (≈ 4 cm^2). A voltammetric scan at 20 mV s^{-1} was applied down to a cathodic potential of -1.9 V (Fig. 10). After the passivation peak corresponding to the electropolymerization of the monomer, the current reached a residual value demonstrating the build-up of an insulating layer. A second voltammetric scan on the same electrode corresponded only to the residual current (Fig. 10). This protective layer was transparent when observed by SEM with Gd/Co alloys (≈ 1 at% Gd). The protective effect of PAN layers grafted onto metals (Cu alloys) was demonstrated in two preceding papers.[28,29] The thickness of the grafted layer was very thin in all cases: it mainly depends on the monomer concentration, about 15 nm with a concentration in AN of 0.2 M and 25 nm with a concentration of 2 M. To obtain complete protection, the so-coated electrodes were dipped in a solution containing 0.5 M PAN dissolved in dimethylformamide. The additional PAN was tangled in the grafted chains and a continuous and dense PAN layer was obtained. The usual test with a drop of a $CuSO_4/H_2SO_4$ mixture demonstrated the effective protective effects. More details about the process are given in ref. 28.

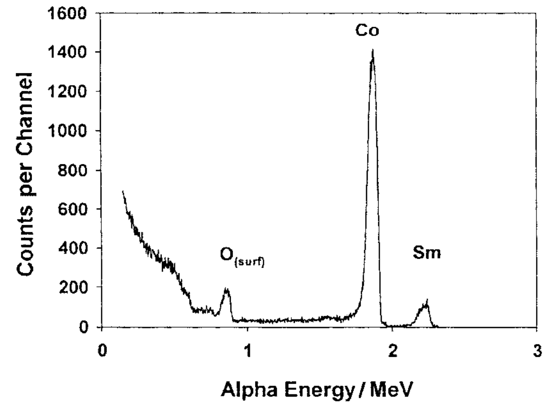

Fig. 9 RBS spectrum of Sm/Co deposited onto a PC/CB cathode.

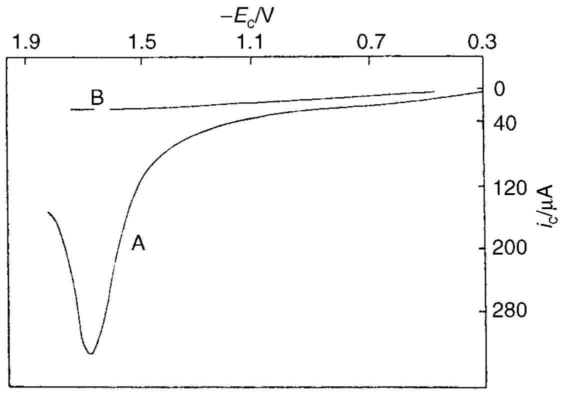

Fig. 10 Cyclic voltammetry recorded on a Gd/Co electrode dipped in acrylonitrile (0.1 M) solution in acetonitrile. (A) First scan, (B) second scan.

Conclusions

In each case, we have reported the best conditions to prepare the quoted alloys, and we have found that composite materials consisting of a conducting polymer and a metal can be prepared by an electrochemical process both in aqueous and in organic solutions. From this fundamental work, it is evident that new materials for technological applications can be foreseen.

The electrodeposition of metallic lanthanides is always a challenge for electrochemistry, whatever the experimental conditions, and we have demonstrated in this paper that conducting polymer cathodes (PE/CB and PC/CB) are suitable for this prospect.

The preparation of lanthanide/transition metal alloys is usually achieved both by quenching and sputtering but the electrochemical process appeared to us an interesting alternative way. The cathodes are easily shaped by extrusion and this would broaden the applications field of such materials.

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