Spontaneous and sustained gold reduction by polyaniline in acid solution

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Spontaneous and sustained reduction and accumulation of elemental gold from chloroauric acid solution by electroactive polyaniline in the leucoemeraldine and emeraldine oxidation states have been demonstrated and explained. A typical polyaniline film can accumulate more than five times its own weight of gold ([Au]/monomer mole ratio > 2) before the reduction rate is substantially retarded by the loss of active surface area due to gold coverage.

(Keywords: polyaniline; oxidation states; gold reduction)

Introduction

Gold is a precious metal that has been in high demand for centuries. Thus, gold recovery from primary and secondary sources, such as leach solutions, electronic scraps and waste electroplating solutions, is an important technology. Although gold recovery by electroplating is well established, other less energy-intensive recovery processes, such as reduction or accumulation by biomass and biomaterials[1–3], by activated carbon[4], by polymeric adsorbents[5] and by electroless plating from chloroauric acid bath[6,7], have also been actively investigated. In this communication, we report on a simple and novel process for the spontaneous and sustained reduction and accumulation of elemental gold on an electroactive polymer surface from an acid gold solution.

The long-established aniline family of polymers[8] has the general formula $[(\text{-B-NH-B-NH-})_y(\text{-B-N=Q=N-})_{1-y}]_x$, in which B and Q denote the C_6H_4 rings in the benzenoid and quinonoid forms, respectively. Thus, the aniline polymers are basically poly(*p*-phenyleneimine-amine)s, in which the intrinsic oxidation state can range from that of the fully reduced leucoemeraldine (LM, $y = 1$), through that of the 50% oxidized emeraldine (EM, $y = 0.5$), to that of the fully oxidized pernigraniline (PNA, $y = 0$). The polymer can achieve its highly conductive state through the protonation of the imine nitrogens (=N– structure) in its EM oxidation state, or through the oxidation of the amine nitrogens (–NH– structure) in the fully reduced LM state[9].

Experimental

In this work, polyaniline (PAN) was first prepared in the EM salt form via oxidative chemical polymerization[9] and then converted to the base form by treatment with 0.5 M NaOH. EM base films, about 12 μm in thickness and 18 cm^2 in surface area (total of both sides), were cast from *N*-methylpyrrolidinone solution[10]. The fully reduced LM film can be obtained by treatment of the EM film with phenylhydrazine[1] while the 75% oxidized nigraniline (NA) film is readily obtained by subjecting the EM film to one cycle of acid/base treatment[11]. The Au concentration remaining in the solution was determined from u.v.–visible absorption spectra by following the $AuCl_4^-$ absorption peak at about 312 nm. Standard chloroauric acid solution, containing 1000 mg dm^{-3} of Au in 0.5 M HCl, was obtained from BDH Chemicals. The surface and interface of the polymer films after Au reduction were analysed by X-ray photoelectron spectroscopy (X.p.s.), carried out on a VG Escalab MkII spectrometer under conditions similar to those reported earlier[12].

Results and discussion

It has been shown that reversible electrochemical oxidation of the LM base form of the polymer in the pH range of about 1 to 4 occurs initially with no deprotonation to give the EM salt; continued oxidation occurs with spontaneous deprotonation to give the PNA base[13]. The reactions are summarized as follows:

$$[\text{-}(C_6H_4)\text{-}N(H)\text{-}(C_6H_4)\text{-}N(H)\text{-}(C_6H_4)\text{-}N(H)\text{-}(C_6H_4)\text{-}N(H)\text{-}]_x \rightarrow [\text{-}(C_6H_4)\text{-}N(H)\text{-}(C_6H_4)\text{-}N(H)\text{-}(C_6H_4)\text{-}N^+(H)\text{=}(C_6H_4)\text{=}N^+(H)\text{-}]_x + (2x)e^- \quad (1)$$

$$[\text{-}(C_6H_4)\text{-}N(H)\text{-}(C_6H_4)\text{-}N(H)\text{-}(C_6H_4)\text{-}N^+(H)\text{=}(C_6H_4)\text{=}N^+(H)\text{-}]_x \rightarrow [\text{-}(C_6H_4)\text{-}N\text{=}(C_6H_4)\text{=}N\text{-}(C_6H_4)\text{-}N\text{=}(C_6H_4)\text{=}N\text{-}]_x + (4x)H^+ + (2x)e^- \quad (2)$$

The oxidized PNA or NA polymer which is formed, readily undergoes reprotonation and reduction in an aqueous acid medium to give rise to a protonated EM salt[14,15]. Reaction (1) has an oxidation potential of about 0.1 V vs. SCE while the oxidation potential for reaction (2) is about 0.7 V vs. SCE. Thus, in an acid gold solution, such as chloroauric acid, the imine nitrogens of the EM base are first protonated by HCl. In the presence of Au(III) ion, spontaneous deprotonation via reaction (2) will result in an increase in the intrinsic oxidation state of the polymer and the reduction of

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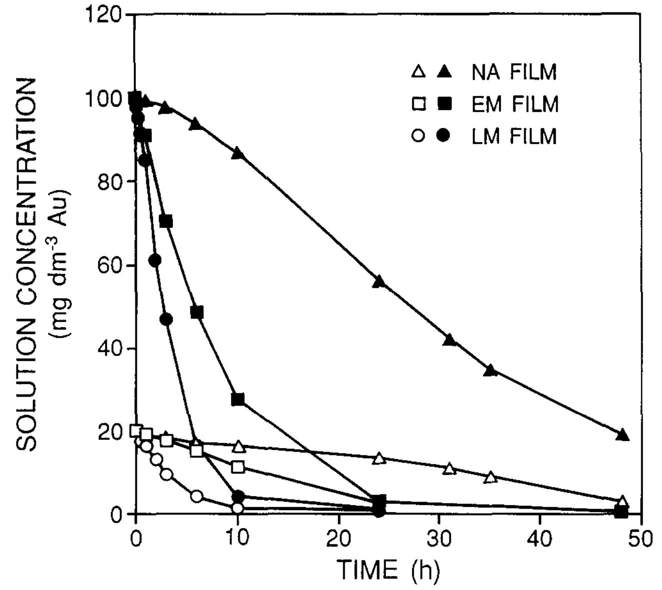

Figure 1 Rates of Au reduction by the LM, EM and NA films in 150 ml of chloroauric acid solution containing either 20 or 100 mg dm^{-3} of Au (pH ≈ 1.3, film dimensions 3 cm × 3 cm × 0.012 mm)

Au(III) to Au(0). The highly oxidized polymer, in turn, is reprotonated and reduced to EM salt in the acid medium, allowing reaction (2) to be repeated. The rates of Au reduction and uptake by the LM, EM and NA films, when each film is exposed to 150 ml of chloroauric acid solution containing either 20 or 100 mg dm^{-3} of Au (pH ≈ 1.3), are compared in *Figure 1.* Thus, with the additional contribution from reaction (1), the LM film exhibits the most rapid rate of Au reduction. On the other hand, however, the requirement for the NA polymer to be protonated and reduced to a structure similar to that of the protonated EM results in a relatively sluggish reduction rate, especially during the initial stage. The data in *Figure 1* further suggest that all three polymers are capable or reducing Au at concentrations substantially below 10 mg dm^{-3}.

Figures 2a and *b* show, respectively, the N1s and Au4f X.p.s. core-level spectra for an as-cast EM film after equilibrating in 150 ml of chloroauric acid solution containing 20 mg dm^{-3} of Au (pH ≈ 2.0) for about 6 h. The surface region analysed has an Au/N molar ratio of about 0.5, as determined from the sensitivity factor corrected N1s and Au4f spectral area ratio. The Au4f spectrum with an Au4f$_{7/2}$ component binding energy (BE) at about 83.8 eV indicates the presence of predominantly Au(0) species. The N1s core-level spectrum is best resolved into three components. The low-BE component at about 398.2 eV is attributable to the imine nitrogens (=N– structure) of the polymer. The main peak at about 399.4 eV is associated with the amine nitrogens (–NH– structure). The high-BE tail, on the other hand, is due to contribution from positively charged nitrogens, as a result of protonation of the imine nitrogens by HCl[12]. The simultaneous presence of the three nitrogen species and Au(0) is consistent with the mechanism of reaction (2).

The intrinsic structure of the polymer after Au uptake is readily revealed by the deprotonated form of the polymer. *Figures 2c* and *d* show, respectively, the N1s and Au4f core-level spectra for a base (0.5 M NaOH)-treated EM film having an Au/N molar ratio of about 1 in the surface region. The N1s core-level spectrum is readily resolved into two major components of about equal area and with BEs at about 398.2 and 399.4 eV, attributable, respectively, to the imine and amine nitrogens of the EM base. The residual high-BE tail is attributable to surface oxidation products[12]. Thus, the intrinsic structure or oxidation state of the EM polymer is not significantly altered by the Au reduction and accumulation process.

It should be emphasized that the present redox couple differs from the conventional anodic and cathodic processes. The polymer 'anode', which is intrinsically oxidized during Au reduction, is readily reprotonated and reduced back to the EM salt in the aqueous acid medium. The hydrolysis reaction[13,14] probably occurs only to a limited extent, as no significant monomer or oligomer absorption was detected in the Au solution, even at a relatively high level of Au uptake by the polymer. The preservation of the polymer 'anode' thus allows, in principle, the continuous reduction of Au in an acid medium. In fact, the polymer film has been observed to readily accumulate more than five times its own weight of Au from the chloroauric acid. Taking into account this high recovery efficiency per unit weight of the polymer substrate, and the fact that Au has already been deposited in its elemental form, it is probably justifiable to recover the metal from the PAN film by thermal decomposition of the latter. The Au reduction process is eventually limited by the 'activation polarization' of the polymeric anode. As Au deposit accumulates on the film surface, the effective contact area between the polymer film and the acid solution is significantly reduced. This phenomenon is also consistent with the observation that the initial rate of Au reduction is increased by more than one order of magnitude when EM powder (particle size, Sauter mean diameter ≈ 30 μm), instead of film, is used for the process.

Finally, it is apparent that the rate of reaction (2) is pH dependent. The rate of Au reduction has indeed been observed to increase substantially as the solution pH is lowered to about 1. However, no significant increase in reaction rate is observed at pH values between ~1 and 0. It should also be noted that as the present Au reduction process is 'electrochemically' coupled with the oxidation

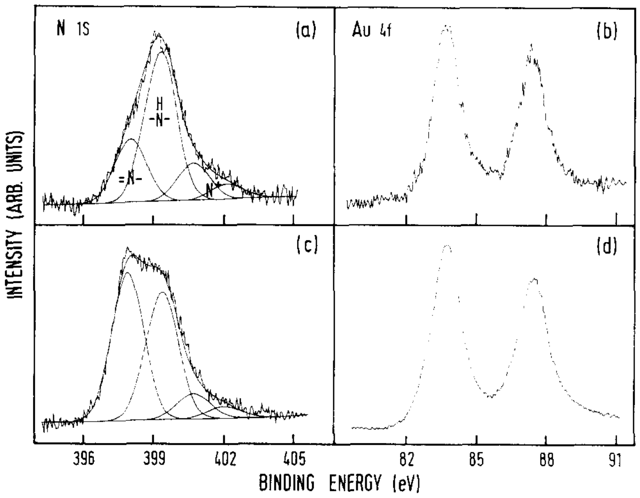

Figure 2 (a) N1s and (b) Au4f core-level spectra of an EM film exposed to chloroauric acid solution containing 20 mg dm^{-3} of Au; (c) N1s and (d) Au4f core-level spectra of similarly exposed EM film after treatment with 0.5 M NaOH

of the aniline polymer, the selectivity of the extraction process in the presence of other metal ions would be determined to a large extent by the reduction potentials of those metal ions in the acid solution. Selectivity based on physicochemical adsorptions on the polymer 'sorbent' probably plays a less important role.

References

1 Hosea, M., Greene, B., McPherson, R., Henzl, M., Alexander, M. D. and Darnall, E. N. *Inorg. Chim. Acta* 1986, **123**, 161

2 Watkins, J. W. II, Elder, R. C., Greene, B. and Darnall, D. W. *Inorg. Chem.* 1987, **26** 1147

3 Kuyucak, N. and Volesky, B. *Biorecovery* 1989, **1**, 189

4 McDougall, G. J. and Hancock, R. D. *Minerals Sci. Eng.* 1980, **12**, 85

5 Wan, R. D. and Miller, J. D. in 'Gold–Advances in Precious Metals Recovery' (Eds N. Arbiter and K. N. Han), Gordon and Breach, New York, 1990, p. 143

6 Luce, B. M. US Patent 3,300,328, 1967

7 McCormack, J. F. US Patent 3,589,916, 1971

8 Green, A. G. and Woodhead, A. E. *J. Chem. Soc.* 1910, 2388

9 Ray, A., Asturias, G. E., Kershner, D. L., Richter, A. F., MacDiarmid, A. G. and Epstein, A. J. *Synth. Met.* 1989, **29**, E141

10 Neoh, K. G., Kang, E. T. and Tan, K. L. *J. Phys. Chem.* 1991, **95**, 10151

11 Kang, E. T., Neoh, K. G., Woo, Y. L., Tan, K. L., Huan, C. H. A. and Wee, A. T. S. *Synth. Met.* 1993, **53**, 333

12 Kang, E. T., Neoh, K. G., Tan, T. C., Khor, S. H. and Tan, K. L. *Macromolecules* 1990, **23**, 2918

13 MacDiarmid, A. G., Yang, L. S., Huang, W. S. and Humphery, B. D. *Synth. Met.* 1987, **18**, 393

14 MacDiarmid, A. G., Manohar, S. K., Masters, J. G., Sun, Y., Weiss, H. and Epstein, A. J. *Synth. Met.* 1991, **41–43**, 621

15 Kang, E. T., Neoh, K. G. and Tan, K. L. *Surface Interface Anal.* 1992, **19**, 33