

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

RTMP COPY

950067-2

OFFICATE
PAP 32

- 1 -

TITLE

REPLACED SHEETS		SG
☒ Description	: paged ...1... to paged ...16...	
☒ Claim(s)	: paged ...17... to paged ...21...	
☒ Drawing(s)	: paged ...11... to paged ...-...	
☒ Abstract	: paged ...22... to paged ...-...	
DATE OF RECEIPT		

Recovery of Precious Metals from Acid Solutions

by Electroactive Polymers

This invention relates to the spontaneous and self-sustained reduction and accumulation of metals, particularly precious metals, for example gold (Au), platinum (Pt) and palladium (Pd), from acid solutions by electroactive polymers for example polyaniline (PAN), polypyrrole (PPY) and their analogues and derivatives, which are capable of assuming a number of intrinsic redox states. A typical polymer film is capable of accumulating more than five times its own weight of a precious metal.

Gold has always been a precious metal in high demand for its decorative and ornamental purposes for centuries. Together with other precious metals, such as platinum and palladium, these metals are of strategic importance for the present day high-technology and electronic industries. Thus, recovery of these precious metals from primary and secondary sources, such as natural ores, leach solutions, electronic scraps and waste electroplating solutions has become an important technology. Recovery of these and other precious metals



- 2 -

by less energy intensive processes, such as gold reduction or accumulation by polymeric adsorbents, by biomass and biomaterials, by activated carbon, and by electroless plating are well documented in the literature. They have been described for example in "Advances in Precious Metals Recovery", edited by N. Arbiter and K.N. Han, Gordon and Breach Science Publishers, N.Y. (1990); and in G.J. McDougall and R.D. Hancock, Minerals Sci. Engng. 12, 85 (1980). Cyanidation, until recently, has been the only alternative to remove small particles of gold from slime on an industrial scale. Gold chlorination and gold extraction from acid solutions have risen to prominence during the last two decades, as this recovery route does not have the adverse environmental effects of cyanidation. Thus, as the demand for gold and other precious metals increases, extraction of these metals from their acid solutions needs to be accomplished with greater efficiency.

In a parallel development, electroactive (conductive) polymers have emerged in the last two decades as a new class of materials with interesting electrical and electronic properties. A number of electrically conductive or semiconductive polymeric materials are known. They have been described, for



- 3 -

example, in "A Handbook of Conducting Polymers", Vols I and II, edited by T. Skotheim, Marcel Dekker, N.Y. (1986). Polymers with conjugated backbone are of particular interest. The electrical conductivities of such materials may be made to undergo a metal-like transition, via a process of chemical or electrochemical doping (oxidation, reduction and protonation etc.) Four main classes of such conjugated polymers have been identified, viz., poly(acetylene) and its derivatives, poly(phenylene) and its derivatives, poly(heterocyclic) polymers, and aniline polymers. Of these polymers, polyaniline (PAN) and polypyrrole (PPY) and their derivatives have been of particular interest because of their high electrical conductivity, environmental stability and interesting intrinsic redox properties associated with the chain nitrogens. The last properties have been studied in detail in E.T. Kang, K.G. Neoh and K.L. Tan, "The Intrinsic Redox States in Polypyrrole and Polyaniline : a Comparative Study by XPS", Surf. Interf. Anal. 19, 33 (1992). Thus, by coupling an increase in the intrinsic oxidation state of these conductive polymers and their spontaneous protonation and reduction in acid solution with a decrease in the oxidation state of the metal, the process is capable of self sustained electroless precipitation of



- 4 -

precious metals in elemental form from acid solution.

Activated carbon was first used as a precipitant for Au in the chlorination process as early as 1880, and for the recovery of gold from cyanide solution in the 1920's. Maximum Au uptake was about 500 mg/g C. The processes have been reviewed by G.J. McDougall and R.D. Hancock, Minerals Sci. Engng. 12, 85 (1980).

The phenomenon of sorption and biosorption has been utilised in the extraction of metallic species from solutions. Living and non-living cells and polymers have been used to concentrate metallic anions from their aqueous environment. The common phenomenon involves rapid and reversible physical/chemical adsorption of metals in the polymer and cellular structure, in combination with complex formation, ion-exchange, and/or microprecipitation.

In U.S. Patent Specification No. 4,769,223, a process is disclosed for removing Au ions from aqueous solution or suspension by biomass derived from the genus *Sargassum* (e.g. *Sargassum natans*), a brown sea-water alga. The maximum metal uptake is in the order of 420 mg per g dry weight of the biomass at pH 2.5. The adsorbed metal is eluted using thiourea and ferric ammonium sulphate as eluant.

In U.S. Patent Specification No. 4,289,531, Pt, Pd



- 5 -

and other precious metals are recovered from aqueous media containing the metal ions by contacting the solution with a proteinaceous material selected from feathers, hair, hoof meal and horn meal. Maximum recoveries of precious metals occur within the preferred pH range of 2 to 3. Typical recovery efficiencies for Pt from 100 ppm chloroplatinic acid are about 70-90 mg Pt/g of contact materials.

In Canadian Patent Specification 2,030,900 cyanide-generating microorganisms, such as algae, bacteria or fungus, are used to leach powder Au ores for low-cost Au recovery and reconcentration. Au recovery is 76-95 ppm vs 0.77 ppm in the absence of culture.

In Japan Kokai Tokyo Koho JP 02080528, HCl solutions containing Ag and Zr ions are contacted with a cationic resin for sorption of the Ag^+ ion.

In Japan Kokai Tokyo Koho JP 02015128, aqueous gel containing persimmon tannin and aldehyde or acid is used for the recovery of noble metals. Thus, aqueous dilute HAuCl_4 solution (pH3) containing 10 ppm Au was contacted for 1h with the gel to recover 98.1% of Au.

In U.S.S.R. Patent Specification 1,556,735, the process involves contacting the solution at various temperatures with a S-containing polymeric sorbent, such as a sulphonated phenolic polymer, to increase the



- 6 -

efficiency of Ag recovery.

In Danish Patent Specification 156075 B, Au is extracted from aqueous solutions containing Au, Cu and Fe in a Thiourea complex from ore extraction by sorption with an acidic cation exchanger (sulphonated polystyrene resin), elution and then reduction. Overall Au recovery efficiency is at 90% for a solution containing 0.5 mg/l thiourea, 0.5 mg/l H_2SO_4 , 0.5% $Fe_2(SO_4)_3$, 160 mg/l Cu and 70 mg/l Au.

In Australian Patent Specification 564754, precious metals (especially Au) in oxides or carbonaceous ores are leached with aqueous cyanide solution and recovered by adsorption on activated C. The loaded C pulp is desorbed in dilute NaOH solution at an elevated temperature and pressure. The hot solution is cooled for precipitation of the precious metal and conventional recovery.

In E. German Patent Specification DD 238033, Pd is selectively separated from acid solutions, especially waste solutions from reprocessing of nuclear fuels, by precipitation with ferrocyanides or sorption on ferrocyanides.

In PCT Int. Appl. WO 8603480, microorganisms, such as algae on glass wool or SiO_2 gel, are applied under controlled conditions of pH and salt concentration to



- 7 -

selectively recover Au, Ag, Pt or Hg. The binding of Au in 10^{-4} M AuCl_4^- solution is high at algae concentration > 1 mg/ml, and is insensitive to pH at 2-9.5. The bound Au^{3+} or Au^+ is eluted as Au^+ by thiourea at 10^{-4} M in 0.01M HCl. The Au recovery for trace Au^{3+} in 0.01M HCl feed solution is 75-100% when passed through a column loaded with algae supported on polyacrylamide.

In Czech Patent Specification 220145, Au and Pt-group metals are recovered from solutions by sorption on polymer gel containing a thiirane group or groups formed by their decomposition by NH_3 . Thus a macroporous 2,3-epithiopropyl acrylate-ethylenedimethacrylate copolymer containing 49% solid and having surface area of $76 \text{ m}^2/\text{g}$ absorbs Au in 24h from a medium containing 2.1M HCl at 100 mg Au/g dried weight without trapping of Cu or other metals.

In West German Specification 3401961A, a cyanide-free hydrometallurgical method is proposed for the recovery of Ag and Au from ores and other raw materials by leaching with thiourea in an acid medium. The precious metals are selectively absorbed on activated C or cation exchanger, eluted with thiourea or acids, and recovered by electrolysis.

In E. German Patent Specification 200792, Pd is recovered from HNO_3 - containing nuclear fuel regeneration



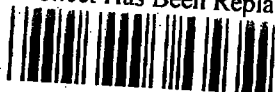
- 8 -

solution by sorption with a chelate-forming ion exchanger. For Pd loading of 45 mg/0.5 g of ion exchanger, the recovery of Pd in the desorption stage is 96%.

In U.S. Patent Specification No. 3,736,126, AuCl_4^- anions are separated from other metals in strong acid solution as they are retained in an adsorption bed of a polymer of lower aliphatic esters of acrylic or methacrylic acid. The absorbed Au can be stripped with dimethylformamide or a mixture of 1M HCl with 2.5 times its volume of Me_2CO .

In U.S.S.R. Patent Specification 1,956,29 Pt is extracted from acid solution by sorption. To increase the effectiveness of the desorption of Pt, an amphoteric resin containing amino acid groups is used as the sorbent.

The present invention is based upon the fact that by coupling a metal reduction process in acid solutions with an increase in the intrinsic oxidation state of an electroactive polymer, for example N-containing polypyrrole, polyaniline or their derivatives, and the subsequent reprotonation and reduction of the intrinsically oxidized polymer in acid media, spontaneous and sustained reduction of precious metals to their elemental form is achieved. Thus, the said polymers are



- 9 -

capable of precipitating, for examples, Au, Pd and Au-Pt alloys from acid solutions containing the respective metal ions. The one-step, energy-free process is capable of recovering precious metals at concentration below 1 ppm. The rate of metal reduction/recovery is dependent on the intrinsic oxidation states of the polymer, the effective surface area of the polymer and the pH of the solution. Thus there is provided a spontaneous and energy-free process for the direct accumulation of precious metals on the polymer surface. The process is self-sustaining and the polymer can readily accumulate more than 500% its own weight of the precious metals before the reduction rate is significantly retarded by the loss of effective surface area due to metal coverage.

According to the present invention, and in one aspect, there is provided a spontaneous and self-sustained process for the recovery of a precious metal from an acid solution containing said metal in solution by treating the said acid solution with an electroactive polymer to cause reduction of the metal in solution to the free metal and allowing the free metal to precipitate from the solution and to accumulate as the reduction progresses.

According to another aspect of this invention there



- 10 -

is provided a process for reducing the oxidation state of a metal, which process comprises contacting an acidic solution of said metal, having an initial oxidation state, with an electroactive polymer and accumulating and recovering said metal, having a final oxidation state lower than said initial oxidation state.

According to yet another aspect of this invention there is provided a process for recovering a precious metal consisting of gold, platinum, palladium and gold-platinum alloys, which process comprises contacting an acidic solution containing said precious metal with an electroactive polymer, and accumulating and recovering said precious metal in metallic form.

The said acid solution may be chosen from mineral acid solutions, inorganic acid solutions and organic acid solutions. The said acid solution may contain said precious metal in ionic form.

The electroactive polymer may be one which is conjugated and derived from a nitrogen-containing monomer or it may be one which contains nitrogen and can exist in a number of intrinsic redox states arising from the chemical nature of the nitrogen, for example from the imine/amine nitrogen ratios in the polymer. The electroactive polymer may be a synthetic aniline polymer or may be derived therefrom or it may be a synthetic



- 11 -

pyrrole polymer or may be derived therefrom. The electroactive polymer may be synthesised by oxidative chemical polymerization or by electrochemical polymerization. The electroactive polymer may be in the form of a powder, film, fibre or gel.

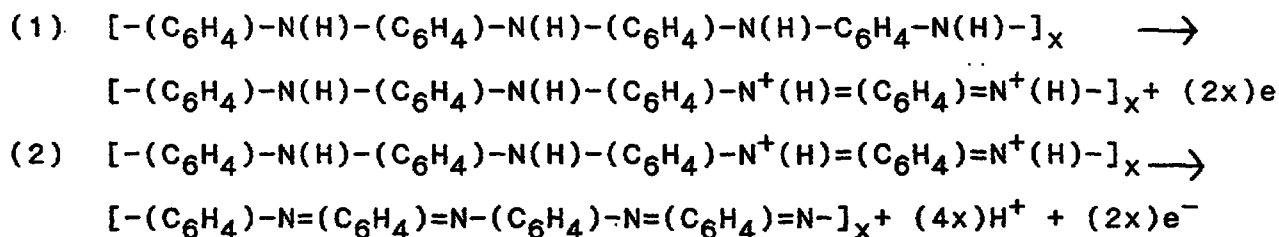
Usually the reduction and precipitation of the precious metal are carried out in an acid solution containing said metal in solution at a pH value of less than 7.

The process may be carried out as a continuous process.

It is well known in the literature that a number of N-containing conjugated electroactive polymers, in particular polypyrrole, polyaniline and their derivatives, can exist in a number of intrinsic redox states. It is further known that these polymers can achieve their highly conductive state either through acid protonation of the imine nitrogen atoms ($=N-$) in their oxidized forms, or through the oxidation of the amine nitrogen groups ($-NH-$) in their reduced states. The oxidation of the reduced states of the two families of polymers, and the subsequent reprotonation and reduction of the polymers at various stages of oxidation in acid solution are utilised for the spontaneous and sustained reduction of precious metals. Thus, using the redox



behaviour of polyaniline in aqueous chloroauric acid solution in a pH range of 1 to 4 as an example:



More recent studies have suggested that treatment of the 75% and fully oxidized polyaniline (nigraniline and pernigraniline, respectively) gives rise not to a protonated nigraniline or pernigraniline, but involves reduction to give rise to a protonated, 50% oxidized emeraldine. This reduction phenomenon allows reaction (2) to be repeated and thus provides a continuous source of electrons for the metal reduction. Similar mechanisms are attributable to the reduction of metal ions by polypyrrole in acid solutions.

It is apparent that the rate of reaction (2) is dependent on the pH of the acid solution. Thus, a substantial increase in the rate of metal deposition is observed when the pH of the acid solution is lowered. The reaction schemes further dictate an enhanced rate of metal reduction for the fully reduced polymers, due to additional contribution from reaction (1). On the other hand, however, the rate of Au reduction is retarded in the more intrinsically oxidized polymer.



- 13 -

EXAMPLES

The following specific examples are provided to illustrate this invention and the manner in which it may be carried out. It will be understood, however, that the specific details given in each example have been selected for purpose of illustration and are not to be construed as a limitation on the invention. In all these examples, the general conditions under which the experiments were conducted were similar, and almost 100% of the initial Au content was recovered in the process. pH typically ranged from 0 to 2.5. Example 1 provides more details on the conduct of the experiment. In the examples where polymer films were used, Au was recovered on the films, while in the case of polymer powder, the contents were centrifuged in order to recover the Au-laden powder.

Example 1

In a preferred experimental scale process, emeraldine base films of size 3 cm x 3 cm (total surface area of 18 cm², both sides) and 12 μm in thickness were exposed to 150 ml of chlorauric acid solutions in several 500 ml Erlenmyer flasks with Au concentrations ranging from 10 to 100 mg dm⁻³. The contents of the flask were



- 14 -

kept homogeneous by slowly stirring with a magnetic stirrer at about 200 rpm. Initial pH typically ranged from about 0 to 2.5. During the reduction process, the concentration of AuCl_4^- remaining in each solution was determined from the UV-visible absorption peak at about 312 nm. At the end of each experiment about 100% of the initial amount of Au was recovered on the film. Figure 1 of the accompanying drawings illustrates graphically the rates of Au reduction by the emeraldine base films in four different chloroauric acid solutions.

Example 2

The rate of Au reduction can be substantially enhanced (by more than 10-folds) when emeraldine base powder (e.g. particle size, Sauter mean diameter of about 30 μm) of comparable weight as the films are used. Figure 2 of the accompanying drawings illustrates graphically the rates of Au reduction by the said emeraldine base powders in five different chloroauric acid solutions.

Example 3

An even more rapid rate of Au reduction is observed in the case of deprotonated polypyrrole powders (containing 25%N-structure) of similar particle size and under the same experimental conditions.

Example 4

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

- 15 -

In a preferred process, the fully reduced leucoemeraldine films are used for the reduction of Au from chloroauric acid solution having Au concentrations ranging from 10 to 100 mg dm⁻³. The fully reduced leucoemeraldine exhibits a substantially higher rate of Au reduction, at least during the initial stage, than its 50% oxidized emeraldine and 75% oxidized nigraniline counterparts.

Example 5

In a preferred process, a fully reduced leucoemeraldine film is subjected to cyclic loading of Au by exposing the film to consecutive batches of chloroauric acid solution containing 100 mg dm⁻³ of Au. The polymer film accumulates more than five times its own weight of elemental gold.

Example 6

In another preferred process, the rates of Au reduction by polyaniline and polypyrrole are substantially enhanced if the pH values of the acid Au solutions are adjusted to 1 or below.

Example 7

In yet another preferred process, either polyaniline or polypyrrole is used for the reduction and accumulation of Pd in nitric acid; or for the reduction and accumulation of Pt in chloroplatinic acid containing also

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

- 16 -

trace amount of chloroauric acid.



- 18 -

a nitrogen-containing monomer.

6. A process according to any preceding claim, wherein the electroactive polymer contains nitrogen and is one which can exist in a number of intrinsic redox states arising from the chemical nature of the nitrogen.

7. A process according to Claim 6, wherein a number of intrinsic nitrogen states arises from the imine/amine nitrogen ratios in the polymer.

8. A process according to any one of Claims 5 to 7, wherein the electroactive polymer is a synthetic aniline polymer or is derived therefrom.

9. A process according to any one of Claims 5 to 7, wherein the electroactive polymer is a synthetic pyrrole polymer or is derived therefrom.

10. A process according to Claim 8 or Claim 9, wherein the said electroactive polymer is synthesised by oxidative chemical polymerization.

11. A process according to Claim 8 or Claim 9, wherein the said electroactive polymer is synthesised by electrochemical polymerization.



- 19 -

12. A process according to any preceding claim, wherein the electroactive polymer is in the form of a powder, film, fibre or gel.

13. A process according to any preceding claim wherein the electroactive polymer is selected from leucoemeraldine, emeraldine, nigraline, pernigraline, ring-substituted and N-substituted aniline polymers of various intrinsic oxidation states, and aromatic amine polymers of various intrinsic oxidation states.

14. A process according to any preceding claim, wherein the reduction and precipitation of the precious metal are carried out in an acid solution containing said metal in solution at a pH value of less than 7.

15. A process according to any one of Claims 1 to 14, which is carried out as a batch process.

16. A process according to any one of Claims 1 to 14, which is carried out as a continuous process.

17. A process for reducing the oxidation state of a metal, which process comprises contacting an acidic solution of said metal, having an initial oxidation



state, with an electroactive polymer and accumulating and recovering said metal, having a final oxidation state lower than said initial oxidation state.

18. A process for recovering a precious metal consisting of gold, platinum, palladium and gold-platinum alloys, which process comprises contacting an acidic solution containing said precious metal with an electroactive polymer, and accumulating and recovering said precious metal in metallic form.

19. A process according to Claim 17, wherein said final oxidation state is zero and said metal is accumulated and recovered in metallic form.

20. A process according to Claim 17 or 18, wherein the concentration of said metal in said acidic solution is less than 1 ppm.

21. A process according to any one of Claims 17 to 20, wherein said electroactive polymer is selected from leucoemeraldine, emeraldine, nigraline, pernigraline, ring-substituted and N-substituted aniline polymers of various intrinsic oxidation states, and aromatic amine polymers of various intrinsic oxidation states.

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

- 21 -

22. A process according to any one of Claims 17 to 20, wherein said electroactive polymer is selected from pyrrole polymers of various intrinsic oxidation states, of deprotonated pyrrole polymers, and of ring- and N-substituted pyrrole polymers of various intrinsic oxidation states.

23. A process carried out according to any one of the preceding claims substantially as herein described and exemplified.