A plasma electrochemistry reactor enabling the rapid and continuous-flow synthesis of gold and platinum group metal (PGM) nanoparticles

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ABSTRACT

The separation and purification of metals of the gold and platinum group (PGM) from slurries obtained from the recycling industry is a major environmental and economic issue. In general, conventional physico-chemical processes pose serious environmental risks and leave short profit margins. Here we present a plasma-based process which is inherently environmentally safer and which is scalable from small to large throughputs. Reduction of four representative PGMs from slightly acidic solutions is demonstrated.

Keywords: gold and platinum group metals, plasma electrochemistry, dielectric barrier discharge, *in situ* spectroscopy, atmospheric pressure plasma

1 INTRODUCTION

PGM extraction from natural ore is highly energy intensive, polluting and very expensive, imposing high threshold values of profitability as well as socio-environmental challenges [1]. Recycling, mainly from automobile catalytic converters, electrical products, and jewelry, has a large potential to lower the threshold values of profitability as well as improve the sustainability and acceptability of the industry. Moreover, it can increase the world supply safety of these "national strategic metals", lowering the economic and political pressures related to the scarcity of the exploitable ores [2]. Recycling of PGMs has been occupying an increasing portion of their world supply over the last decade, reaching 36% for platinum for example in 2013 [3].

Even recycling though necessitates purification final steps that are expensive and polluting. Indeed, the refining and separation of the individual PGMs involve several complex and tedious hydrometallurgy processes which involve some energy intensive thermal treatments resulting in the release of large quantities of CO_2 equivalents, as well as large volumes of very acidic solutions or organic solvents resulting in important safety and disposal issues [4, 5]. These processes require large equipment and capital investments.

Plasma electrochemistry could lead to new paradigms in the field of PGM hydrometallurgy, having the potential to reduce both the environmental and the economic costs of PGM refining. This step could therefore be performed by local or regional PGM-recycling companies, bringing recycling processes closer to the "urban mining potential" and thereby cutting on waste materials transportation costs.

Recently-introduced atmospheric pressure plasma electrochemistry is particularly attractive for industrial processes. A plasma, a gas ionised by electrical means, is generated between an upper conductive electrode and the surface of a solution of dissolved PGMs (or other noble metals like gold) to be purified. The general principle of plasma reduction/synthesis is schematised in Figure 1a. In brief, a gas such as hydrogen is flown over an aqueous solution of PGM salts; there, it gets partially ionised by an electric field, becoming a plasma. It is composed of electrons as well as positive ions and excited atoms mostly of the feed gas but also of oxygen and nitrogen present as residuals. Electrons can in principle directly reduce the metal ions into metallic nanoparticles near the surface of the solution. However, recent results point to a more complex process involving dissolved reactive species produced by the interactions between the different species present in the plasma and the liquid. The produced metallic nanoparticles can easily be sedimented by centrifugation then dried and melted into ingots under inert atmosphere.

The dielectric barrier discharge (DBD) type of reactor presented here is well adapted to the treatment of large surfaces, hence large volumes of solution. It includes fluid circulation capacity for the treatment of small to large volumes of solution hence the production of small to large amounts of particles. In-situ, real-time ultraviolet-visible (UV-Vis) absorbance spectroscopy of the circulating solution/suspension is integrated for the monitoring of the process. The modular configuration and the materials are optimised for high purity, efficient heat management and easy replacement of worn or contaminated parts. The tabletop version presented here would be adequate for jewelry or dentistry waste recycling but could be scaled-up and/or paralleled for larger productions (e.g. catalytic waste).

Four different PGMs (platinum, palladium, rhodium and iridium) were successfully reduced and extracted from their solution both with and without the suspension stabilizer/growth inhibitor dextran (a saccharide). The different reduction efficiencies at the same conditions or alternately the different conditions required for the most efficient reduction of the different metals point to a strong potential for the separation of pure metals from solutions of their mixture and of impurities. Differences between PGMs and gold nanoparticles productions are highlighted. For a specific description of the gold-related results, the reader is refered to paper 887 of the present proceedings.

2 MATERIALS AND METHOD

2.1 Plasma synthesis equipment and in situ spectroscopy

Figure 1b shows the main internal parts of the DBD reactor that was used for the synthesis of PGMs nanoparticles. The metal salt solution is circulated by an external pump through a long and narrow (~1 cm) channel (arrows 1 to 4 to 5 on the drawing) then through an in-line quartz spectroscopy cell (Spectrosil Quartz, Starna Cells) (arrows 5 to 6). Hydrogen gas (99.999%, Linde Canada) is flown perpendicularly through a small gap (~3 mm) over the channel. It is ionized by an alternating electric field coming from above through a dielectric barrier which is constituted of the bottom wall of two successive quartz cells. These cells contain flowing tap water which constitutes a liquid, self-cooling/reguvenating upper electrode. A high and alternating sinusoïdal voltage (7.5 kV amplitude, 25 kHz frequency) is applied to that liquid electrode through corrosion-resistant metallic tubes. The gold solution is electrically grounded by corrosion-resistant thermocouple shields (omegalloy, OMEGA Environmental) situated away from the discharge. The whole system is built modularly with acid-resistant polymers and allows the quick and easy replacement of worn or contaminated parts. It is described in more details elsewhere [6].

The UV-Vis absobance of the flowing solution/suspension is measured through the in-line quartz cell at the exit of the plasma region by a UV-Vis spectrometer (HR4000CG-UV-NIR, Ocean Optics) coupled to a fiber optics halogen light source.

2.2 Preparation of metal ions precursors

All PGM metal chloride precursors were purchased from Sigma-Aldrich and were of purity > 99%. Palladium (II) chloride, chloroplatinic acid hydrate (38% Pt basis), rhodium (III) chloride and iridium (III) chloride hydrate were used for the experiments. The precursor solutions were prepared with and without surfactant. The PGM metal chloride precursors were dissolved in 20 mL of nanopure water (Barnstead, 18.2 MΩ) to a concentration of 1 mM.

Rhodium solutions had to be heated in order to dissolve the metal precursor. Chlorhydric acid (37%, Anachemia Canada) was used to dissolve the palladium and rhodium precursor. For the solutions containing surfactant, dextran (M.W. 5 kDa, Carbomer Inc.), was added to a concentration of 1 mM to serve as a steric stabilizer of the nanoparticles growth. A UV-visible spectrum was taken on every precursor solution, prior to any experiment. The pH of the final solutions was measured. Solutions were kept at 4 °C until used.
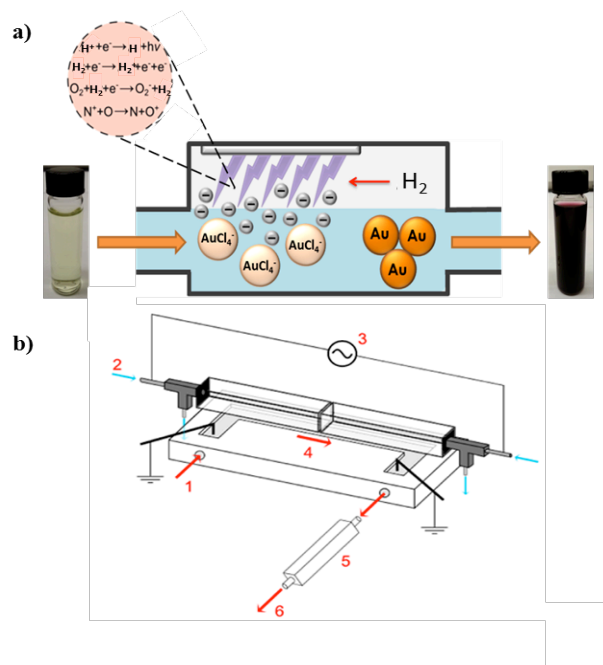

Figure 1: a) Schematic representation of nanoparticles synthesis by plasma electrochemistry; b) schematic representation of the internal parts of the modular DBD continuous flow reactor.

2.3 Nanoparticle plasma synthesis procedure: in situ monitoring profile

The synthesis procedure was as follows. The 20 mL of solution was closed-loop circulated through the system for the entire period of treatment which correponded to the duration of application of the high and alternating voltage (7.5 kV amplitude, 25 kHz frequency) and was fixed to 10 min. Meanwhile, 100 mL/min of hydrogen was kept flowing through the discharge gap.

UV-Vis absorbance spectra were acquired at regular intervals of time (typically 5 s) over the 450 nm to 650 nm wavelenght range to evaluate the possibility of monitoring the reduction process. In fact, surface plasmon absobance peaks for PGMs appear in the UV for very small nanoparticles and are therefore difficult to distinguish from the solvated ions related peaks. However, they are well shifted in the visible part of the spectrum for particles larger than a few tens of nm. Another difficulty resides in the strong dependance of the absorbance on the oxidation state

of the nanoparticles' surface which itself is dependent on the pH in an aqueous solution. Even slightly acidic solutions are detrimental to the observation of SPR peaks [7, 8]. Nevertheless, real-time monitoring has been succesfuly performed for Pt and Pd (figure 2) although no quantitative information could be gathered as will be discussed below.

2.4 Analytical methods

POST-SYNTHESIS UV-VIS SPECTROSCOPY

After plasma synthesis, 1 mL of the suspensions was analyzed by ex-situ UV-Vis absorbance spectral measurements (200 to 800 nm, UV-1601, Shimadzu) in a quartz cell (path length: 10 mm), in order to follow the stability of the nanoparticles suspensions over time. Palladium, platinum and rhodium suspensions were diluted (1/10) in nanopure water (Barnstead, 18.2 MΩ) before acquiring the UV-vis spectra.

SIZE MEASUREMENTS (DLS)

The hydrodynamic diameters of the PGM nanoparticles were evaluated by dynamic light scattering (DLS; Malvern Zetasizer, 173°) at 25° C from the average of three measurements. The plasma treated PGM suspensions were diluted in water (1/10) for the measurements. The viscosity and refractive index of water were set to 0.8872 cp and 1.33 respectively. For platinum, palladium, rhodium and iridium, the refractive indexes were set to 4.500, 1.800, 2.140 and 1.570 respectively.

QUANTIFICATION (AES)

5 mL of each suspension was transferred in a 15 mL centrifugation tube and was then centrifuged (3000 g, 15 min). 1 mL of the supernatant was collected in duplicate and digested with aqua regia and hydrogen peroxide (30%, Sigma-Aldrich) at 115 °C until the suspensions turned clear and colorless. The concentration of residual ions was measured by microwave plasma atomic emission spectroscopy (MP-AES 4100, upgraded to 4200).

3 RESULTS AND DISCUSSION

Different conditions have been tested in order to determine a common set of parameters adequate for the synthesis of the four different types of nanoparticles. Only the final selection will be discussed here: 1 mM of metallic salt with and without 1 mM of Dextran; discharge duration of 10 min; 7.5 kV, 25 kHz applied voltage. Most importantly, hydrogen was chosen as the feed gas. Indeed, hydrogen plasma was found not only to greatly facilitate the reduction of Pd, Rh and Ir but to be essential for the reduction of Pt. It would seem that other reactive species than hydrogen are involved in the reduction of PGMs, which doesn't seem to be the case for gold.

Stronger heating of the solution during hydrogen plasmas (compared to Ar plasma) could also be involved, particularly with Pd for which reduction seems possible only at high temperatures (~80°C).

Contrary to the case of gold for which dextran is essential as a nucleation site, and contrary to what the curves of figure 2 suggest, dextran has proved to be detrimental to the reduction of the PGMs at least in terms of efficiency. Table 1 shows the reduction efficiencies of the four metals as measured by AES, with and without dextran.

Metal	% With dextran	Without dextran
Pt	17±1	25.3±0.3
Pd	37±2	80.7±0.2
Rh	67±1	74±1
Ir	23±1	23±1

Table 1: Effect of dextran on the reduction efficiency of plasma-treated solutions of PGMs.

For Pd, the presence of dextran more than halfed the reduction efficiency although the curves in figure 2 seem to indicate the contrary. Here, the great sensitivity of the SPR peak of Pd to surface states/environment prevents any quantitative comparison between the different curves from figure 2. The effect on the curves related to Pt is less dramatic but similar as is the effect of dextran on the reduction efficiency of Pt. Dextran had no significant effect on the reduction efficiency of both Rh and Ir. In general, the process proved efficient for the reduction of Pd and Rh although not as much as what has been obtained for Au (99.8%). Reduction efficiencies of Pt and Ir must be improved.
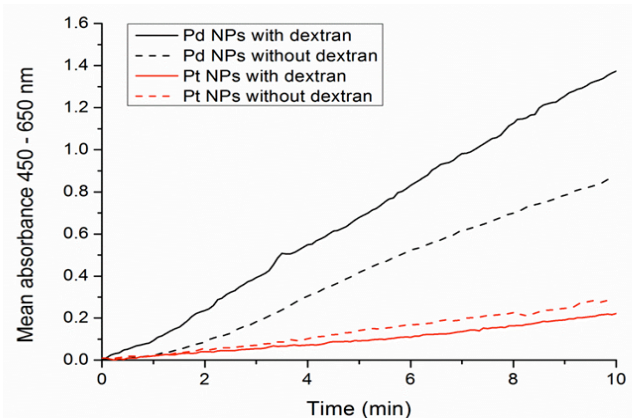

Figure 2: Evolution of the nanoparticles-related UV-Vis absorbance during the plasma reduction of dissolved Pt and Pd salts with and without dextran.
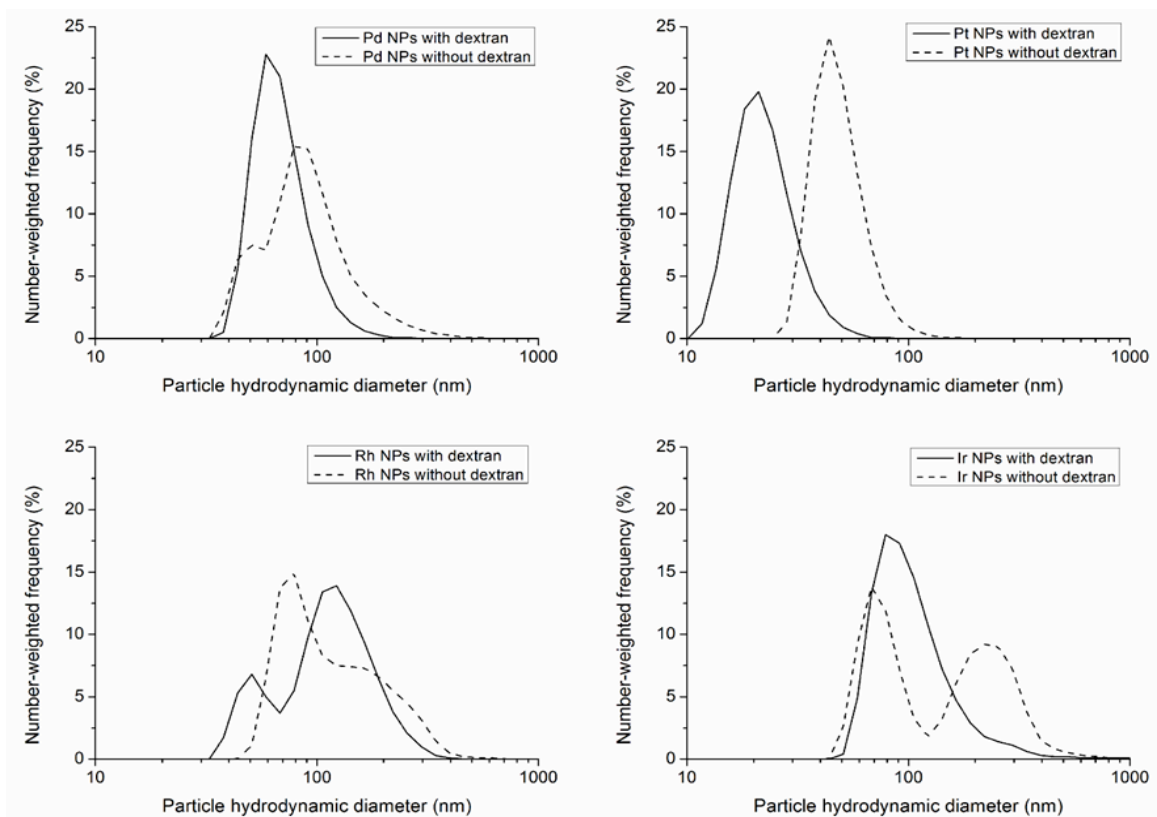
Figure 3: Number-weighted DLS size measurements of the diluted plasma-treated solutions of PGM with and without dextran.

The effect of dextran was very different on the size distributions as can be seen on figure 3. As expected, smaller nanoparticles were generated and unimodal distributions were obtained by adding dextran, except for Rh. On the contrary, dextran-less particles tended to be distributed bimodaly except for Pt. This is also expected as dextran prevents agglomeration which obviously occurs for Pd, Rh and Ir in the absence of surfactant.

4   CONCLUSION

The DBD atmospheric pressure plasma process presented here was able to efficiently reduce palladium and rhodium and also platinum and iridium although with a lesser efficiency. Particles with sizes varying from a few tens to a few hundreds of nanometers could be produced and easily sedimented by centrifugation. The potential of the technique is only emerging and further work will certainly bring improvments in efficiency, particle size control as well as selectivity. Identification of the reactive species and temperature control are the next lead.

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