A method for coating a polymer inclusion membrane with palladium nanoparticles

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ABSTRACT

The preparation of palladium nanoparticles on the surface of a polymer inclusion membrane (PIM) consisting of 30 wt% di-(2-ethylhexyl)phosphoric acid and 70 wt% poly(vinyl chloride) is described. The Pd(II) ion was firstly extracted into the membrane via cation-exchange and then subsequently reduced to form clusters of palladium nanoparticles on the membrane surface. The reducing agents investigated were $NaBH_4$, trisodium citrate, sodium formate, and L-ascorbic acid. Best results were obtained with L-ascorbic acid which at pH 2.0 formed a uniform layer of palladium nanoparticle clusters on the surface of the PIM with an average nanoparticle size of 38 nm. Factors such as pH, temperature and intensity of mixing of the L-ascorbic acid solution, reduction time and Pd(II) loading of the PIM were found to have a significant influence on the surface coverage and size of the palladium nanoparticles.

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1. Introduction

The preparation of palladium nanoparticles (PdNPs) has gained particular interest due to their unique optical, electronic and catalytic properties [1]. These unique properties have led to research into the potential applications of PdNPs such as in biological labeling [1,2], hydrogen storage [3–5], catalytic activity toward CO oxidation [6], and in fuel cells [7–9]. PdNPs infused in a polymer film allowed efficient oxygen scavenging in the production of nitrogen of high purity [10]. Various methods for the preparation of PdNPs have been studied and they can be classified into two main groups, i.e., template-free self-assembly methods and linear template methods [11,12]. As the name suggests, template-free self-assembly methods involve the reduction of palladium ions with reducing agents without any template. The agglomeration of NPs is prevented by the addition of stabilizing agents [13,14]. The linear template methods use a template to grow PdNPs in the presence of a suitable reducing agent. The templates used range from biomolecules (e.g., DNA or proteins), inorganic nanowires and nanotubes (e.g., carbon nanotubes) and other solid substrates [11,12,15]. The use of a polymer as a linear template for the preparation of PdNPs has also been widely studied. The polymers used include Nafion [16,17], poly(vinyl alcohol) (PVA) [18] and poly(N-vinyl-2-pyrrolidone) (PVP) [19].

A polymer inclusion membrane (PIM) is a type of liquid membrane that is formed by casting a solution containing an extractant, a base polymer and, if necessary, a plasticizer and/or modifier and allowing the solvent to evaporate. This produces thin, flexible and stable membranes that have gained considerable interest due to their capability to selectively extract both metallic and non-metallic species [20–35]. The common base-polymers used are cellulose triacetate (CTA) and poly(vinyl chloride) (PVC) [20]. The extractant, often referred to as the carrier, is a complexing agent or an ion-exchanger (e.g., Aliquat 336, Cyanex 272 and di-(2-ethyl-hexyl) phosphoric acid (D2EHPA)). A plasticizer (e.g., 2-nitrophenyloctyl ether (2-NPOE)) and/or modifier (e.g., a long chain alcohol) can be added to the membrane composition to increase the membrane softness, flexibility, permeability, and the compatibility of the membrane components [20,30].

In previous studies, we successfully prepared gold nanoparticles (AuNPs) [36] and silver nanoparticles (AgNPs) [37] on the surface of PVC-based PIMs and established that the PIM polymer and extractant allowed immobilization of metal nanoparticles on the membrane surface with practically none being formed within the bulk membrane. Through the membrane composition and the reducing conditions it was possible to control the size of the metal nanoparticles. Thus, it was of interest to study the possibility of using this approach involving a PIM template for producing PdNPs. The PIM template consisted of a PVC-based PIM containing D2EHPA as the extractant to extract Pd(II) cations which were then reduced to produce PdNPs. Several reducing agents for Pd(II) have been studied including L-ascorbic acid which is known to reduce Pd(II) in aqueous solutions to form palladium nanocrystals [38]. To our knowledge, there has not been any other report on the synthesis of PdNPs using a Pd(II) loaded PIM as the template.

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2. Experimental

2.1. Reagents and solution preparation

D2EHPA (purity 97 wt.%, Aldrich), high molecular weight powdered PVC (Fluka), tetrahydrofuran, THF, (Chem-supply, Australia), and acetone (Chem-supply, Australia) were used as received. Pd(II) calibration standards were made from a 999 ± 4 mg L^{-1} Pd(II) Atomic Absorption Spectrometry (AAS) standard solution (Fluka Analytical).

The aqueous Pd(II) solutions for membrane extraction were prepared from $Pd(NO_3)_2 \cdot xH_2O$ (Sigma-Aldrich). The exact Pd concentration in these solutions was determined by AAS. Aqueous solutions of L-ascorbic acid (Sigma), trisodium citrate (Chem-supply, Australia), citric acid (Ajax Finechem, Australia), and sodium borohydride (Ajax Finechem, Australia) were used for the reduction of Pd(II). The pH of L-ascorbic acid solutions was adjusted with 0.10 mol L^{-1} HNO_3 or NaOH (Chem-supply, Australia) solutions.

Deionized water (18 M Ω cm, Millipore, Synergy 185, France) was used for the preparation of all aqueous solutions.

2.2. Instrumentation

AAS (Hitachi Z-2000 Series polarized Zeeman atomic absorption spectrometer, Japan) was employed to determine aqueous Pd(II) concentrations.

Extraction experiments were conducted in glass jars positioned in a thermostated orbital mixer incubator (Model OM11, Ratek, Australia) at temperatures of 20 °C and above and on a platform orbital mixer (Model OM6, Ratek, Australia) located in a commercial refrigerator (CLEGG, temperature controller E5CN, OMRON, Australia) for temperatures below 20 °C.

Visual examination of the membranes and membrane thickness measurements were carried out using a Motic SMZ-140 stereo microscope (Motic, China) with $60\times$ magnification in combination with a MoticCam 1000 microscope camera (Motic, China).

Scanning electron microscopy (SEM) and energy dispersive spectrometric (EDS) analysis were carried out using an FEI Quanta 200 F instrument (FEI, USA) equipped with a silicon drift detector (Inca X-act, 10 mm and 126 eV) and running INCASuite version 4.15 software (Oxford Instruments Analytical Ltd., USA). Measurements were carried out at 20 kV in high-vacuum. The resolution of this instrument as stated by the manufacturer is between 1.2 nm and 3.0 nm at 30 kV and 1 kV, respectively. Measurements were conducted at 30 kV and the size of the PdNPs was assessed using Scandium 5.0 software (Olympus Soft Imaging Systems, Japan).

The UV–visible spectrum of the optimized membrane containing PdNPs was obtained with a UV–Visible spectrophotometer (Evolution 220, Thermo Scientific, USA). Measurements were made in reflectance mode as the PdNPs were concentrated on the membrane surface.

2.3. Membrane preparation

Throughout this paper, PIM composition is expressed in mass percentage (wt.%). Membranes containing 20% and 30% D2EHPA with a total mass of 400 mg were prepared by dissolving the appropriate masses of D2EHPA and PVC in 5 mL THF. The solution was then poured into a 7.5 cm diameter glass ring positioned on a flat glass plate which had previously been cleaned with acetone. The mixture was covered with filter paper and a watch glass and the solvent was allowed to evaporate over 24 h. This produced a transparent and flexible membrane. A circular membrane segment (mass 60 ± 3 mg, thickness 50 ± 5 μm) was cut from the centre of the membrane with a circular steel punch of diameter 3.5 cm and used in the extraction experiments.

2.4. Pd(II) extraction

Membrane segments were immersed in 100 mL of a freshly prepared $Pd(NO_3)_2$ solution (50 mg L^{-1} Pd(II), natural pH 3.0) in glass jars. Extraction experiments were also conducted at pHs 1.0 and 2.0 where the pH was adjusted by the addition of 0.1 M HNO_3. The jars were shaken under controlled temperature conditions using a platform orbital mixer at 150 rpm and samples (0.2 mL) were removed at predetermined time intervals. These samples were diluted to 4 mL with 0.10 mol L^{-1} HCl and the Pd(II) concentration was determined by AAS.

2.5. Reduction of Pd(II) and SEM analysis

Pd(II) loaded membrane segments were immersed in glass jars containing 100 mL of 0.10 mol L^{-1} of the individual reducing reagents in deionized water. The jars were shaken using a platform orbital mixer at 150 rpm for 24 h. The membrane segments were then removed from the solutions, rinsed with deionized water and allowed to dry in air. A square segment (1×1 cm) was cut from the centre of each circular membrane segment and mounted on a carbon tab (12 mm) with a pin type scanning electron microscopy (SEM) mount (12.6 mm). The images of the surface and the cross-section of the membrane were captured using SEM. The average size of the PdNPs was determined by Scandium 5.0 software and this involved the averaging of the size of 10 different PdNPs from 5 different spots on the membrane surface.

The effect of the L-ascorbic acid concentration (0.05, 0.10, 0.15, and 0.20 mol L^{-1} at pH 2.0) and the pH of its solution (1.0, 2.0, 2.6 and 3.0 in the case of 0.10 mol L^{-1} L-ascorbic acid) on the reduction process were studied by exposing Pd(II) loaded PIMs to appropriately prepared L-ascorbic acid solutions for 24 h.

The influence of the shaking rate on the formation of PdNPs at 20 °C was studied by immersing Pd(II) loaded PIMs in 0.10 mol L^{-1} L-ascorbic acid solutions at pH 2.0 for 24 h using shaking rates of 0 (i.e., static solution), 50, 75, 100, and 150 rpm.

3. Results and discussion

3.1. Pd(II) extraction and membrane loading

PVC membranes containing 20% or 30% D2EHPA were loaded with Pd(II) by immersion in Pd(II) solutions until equilibrium between the membrane and the solution had been attained. It was found necessary to use a freshly prepared Pd(II) solution since the solution "aged" with time. The "aging" process involved the slow formation of hydroxocomplexes [39]. If solutions were kept for longer than 24 h, a precipitate was observed.

The extraction of Pd(II) with D2EHPA occurs through a cation exchange mechanism between the Pd(II) cation and the H^+ ion associated with D2EHPA. Extraction curves showing the increase in the loading of Pd(II) in the PIM (mg Pd/g PIM) with time are presented in Fig. 1(a). Rapid extraction was observed in the early stages of the process and equilibrium was reached in a few hours. As expected, the PIM containing 30% D2EHPA showed a higher initial extraction rate and higher membrane loading capacity (0.34 meq g^{-1}) than the PIM containing 20% D2EHPA (loading capacity, 0.20 meq g^{-1}). From these initial extraction experiments, the PIM containing 30% D2EHPA was chosen for the subsequent studies.

The effect of solution pH on the extraction of Pd(II) was studied and extraction curves obtained at different pH values are shown in Fig. 1(b). The rate and extent of extraction increased with increasing solution pH which agrees with results reported by St. John et al. [40] for metal ion extraction into PIMs containing D2EHPA. At pH values greater than 3, D2EHPA-based PIMs became unstable since the pK_a of D2EHPA is approximately 3.5 [41] and its ionization at pH values greater than 3 leads to its leaching into the aqueous phase [40]. Thus, Pd(II) solutions