



Effect of $\text{Al}(\text{NO}_3)_3$ on suppression of the reduction of Ag ions in a poly(vinylpyrrolidone)/ AgClO_4 complex membrane

Ki Wan Yoon, Sang Wook Kang*

Department of Chemistry, Sangmyung University, Seoul 110-743, Republic of Korea

HIGHLIGHTS

- Incorporation of $\text{Al}(\text{NO}_3)_3$ into poly(vinylpyrrolidone)/ AgClO_4 complex.
- The use of $\text{Al}(\text{NO}_3)_3$ to suppress the reduction of Ag^+ ions originating from the AgClO_4 salt.
- Formation of silver nanoparticles in PVP/ AgClO_4 film in the absence of $\text{Al}(\text{NO}_3)_3$.

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ABSTRACT

Our previous study showed that the incorporation of $\text{Al}(\text{NO}_3)_3$ into a polymer/ AgBF_4 complex could enhance the long-term stability of film capable of showing the antibacterial effect and olefin/paraffin separation, because the Ag^+ ions were not easily converted into Ag nanoparticles. In this study, the effect of $\text{Al}(\text{NO}_3)_3$ on the suppression of the reduction of the Ag^+ ions originating from the AgClO_4 in the polymer was investigated, because AgClO_4 is more cost effective than AgBF_4 . As a result, the use of $\text{Al}(\text{NO}_3)_3$ was found to suppress the reduction of Ag^+ ions originating from the AgClO_4 salt, whereby the stability of the Ag^+ ions was largely enhanced even though it is well known that these ions are readily reduced to Ag nanoparticles. Actually, Ag nanoparticles were shown to easily form from the poly(vinylpyrrolidone)/ AgClO_4 complex in the absence of $\text{Al}(\text{NO}_3)_3$, as confirmed by transmission electron microscopy (TEM) and UV–vis spectra.

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1. Introduction

The Ag ion and Ag nanoparticles have attracted much interest due to excellent anti-bacterial characteristics [1,2]. Especially, it was well known that the anti-bacterial ability of Ag ion was much higher than that of Ag nanoparticles. Furthermore, Ag ions have been utilized as a carrier for olefin/paraffin separation since they could be reversibly interacted with olefin molecules [3–6]. In detail, when a olefin/paraffin mixture is passed through the membrane containing Ag ion carriers, olefin molecules that have combined with the carriers can be much more easily transported than uncombined molecules by the solution–diffusion mechanism and facilitated transport. Similar phenomena were also observed in facilitated CO_2 transport membranes to utilize the specific carriers [7–9]. In this case, the carriers were fixed within a polymer matrix and the complexed molecules passed through the membrane by transportation from carrier to carrier [10–12]. Consequently, the

silver ions (Ag^+) from silver nitrate (AgNO_3), silver tetrafluoroborate (AgBF_4), and silver perchlorate (AgClO_4) were generally recognized as typical anti-bacterial agents or olefin carriers [11,13–17]. However, the disadvantage of silver ions is that they are readily reduced to silver nanoparticles with time, thereby resulting in a deterioration of the anti-bacterial or carrier properties. In particular, AgBF_4 , which mostly exists in the free ionic form, readily aggregated to silver nanoparticles even under conditions of darkness [18]. Very recently, attempts were made to improve the long-term stability of the olefin separation membrane by adding $\text{Al}(\text{NO}_3)_3$ to POZ/ AgBF_4 complex membranes. These membranes showed significant long-term stability for more than 14 days, and the color of the membrane film remained white for more than three months. Based on this research, we determined that $\text{Al}(\text{NO}_3)_3$ functions by suppressing the reduction of the silver ions to silver nanoparticles, because of the strong interaction of the Al ions with the F ions of BF_4^- . Consequently, the free NO_3^- anions are available to interact with the Ag ions, and this resulted in the reduction of silver ions in the membrane being restrained [19]. Very recently, poly(ethylene oxide) (PEO)/ AgBF_4 / $\text{Al}(\text{NO}_3)_3$ complex

* Corresponding author. Tel./fax: +82 2 2287 5362.

E-mail address: swkang@smu.ac.kr (S.W. Kang).

membrane presented a selectivity of 10 and mixed-gas permeance of 20 GPU in separation performance as well as long-term stability for more than 10 days, indicating that Ag ions remained constant with time. This excellent long-term stability was attributable to the electrostatic interaction between the Al ions and BF_4^- anions [20]. However, the use of these membranes or anti-bacterial films for practical applications would require more affordable silver salts, such as AgClO_4 and silver trifluoromethanesulfonate (AgCF_3SO_3). In addition, the $\text{Al}(\text{NO}_3)_3$ would be required to interact effectively with the silver salt. Therefore, in this study, our group decided to investigate the suitability of AgClO_4 in combination with $\text{Al}(\text{NO}_3)_3$ as an effective anti-bacterial agents or olefin carrier and its ability to promote long-term stability for practical applications.

2. Materials and methods

2.1. Chemicals

Silver perchlorate (AgClO_4 , anhydrous, 97%), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99%), and poly(vinylpyrrolidone) (PVP, Mw 1.3×10^5 g/mol) were purchased from Aldrich Chemical Co. All chemicals were used as received.

2.2. Characterization

The morphology of the silver nanoparticles, which were produced by the reduction of silver ions, was observed by using transmission electron microscopy (TEM, FEI Cyrotecni F20G2), operating at an accelerating voltage of 200 kV. Samples for TEM images were prepared by dropping a small amount of an aqueous solution containing PVP and Ag^0 onto a standard TEM carbon-coated copper grid. The UV–vis absorption spectra (from 300 to 700 nm) were obtained using a Cary 5000 UV spectrophotometer with a 5 nm resolution to confirm the formation of Ag nanoparticles in PVP solutions. The weight loss was confirmed using thermogravimetric analysis (TGA, TGA Q50, TA Instrument) of the nanocomposite samples in flowing N_2 .

2.3. Preparation of PVP/ AgClO_4 / $\text{Al}(\text{NO}_3)_3$ electrolyte film

In this study, polymer electrolyte membranes consisting of a PVP/ AgClO_4 / $\text{Al}(\text{NO}_3)_3$ active layer were prepared by a simple method by dissolving AgClO_4 and $\text{Al}(\text{NO}_3)_3$ in an aqueous solution containing 20 wt% of PVP.

The molar ratio of the carbonyl group to silver ions was fixed at 1:1, and the molar ratio of $\text{Al}(\text{NO}_3)_3$ to silver ions was fixed at 0.1. Membranes were fabricated by coating a commercial macroporous polysulfone membrane support (Toray Inc, Japan) with the resulting solution using an RK Control Coater (Model K202, Control Coater RK Print-Coat Instruments Ltd, UK). The PVP/ AgClO_4 / $\text{Al}(\text{NO}_3)_3$ complex membrane that was prepared in this way was completely dried in a vacuum oven for one day at room temperature.

2.4. Preparation of silver nanoparticles

The addition of AgClO_4 to aqueous polymer solutions leads to the slow reduction of silver ions to silver nanoparticles observed as a gradual yellowish coloration of the membrane film.

The silver nanoparticle membrane was fabricated by dissolving AgClO_4 in a water solution containing 20 wt% of PVP as described above. After adding $\text{Al}(\text{NO}_3)_3$ to the PVP/ AgClO_4 complex, the silver salt polymer solution was coated onto the macroporous polysulfone membrane support (Toray Inc, Japan) using an RK Control

Coater (Model K202, Control Coater RK Print-Coat Instruments Ltd, UK). Then, the PVP/ AgClO_4 complex membrane was exposed at room temperature for two weeks.

3. Results and discussion

3.1. Formation of Ag nanoparticles

In Fig. 1(a), it can be seen that the PVP/ AgClO_4 complex film showed a change of color from white to dark after exposure at room temperature over more than 4 days, indicating that the silver ions were reduced to silver nanoparticles within the polymer matrix. On the other hand, Fig. 1(b) presents that the PVP/ AgClO_4 / $\text{Al}(\text{NO}_3)_3$ complex film nearly remained white after exposure at room temperature for more than 4 days, indicating that the silver ions were quite stable in the polymer matrix. Fig. 2(a) showed that the PVP/ AgClO_4 film had a yellowish color after exposure at room temperature for more than 12 days, indicating that many of the silver ions were reduced in the polymer matrix, suggesting that most of the silver ions were converted to silver nanoparticles. Sequentially, Fig. 2(b) showed that only a small amount of silver nanoparticles was generated in the presence of $\text{Al}(\text{NO}_3)_3$ after 12 days. These results confirmed the effectiveness of $\text{Al}(\text{NO}_3)_3$ to suppress the reduction of silver ions.

3.2. TEM image of Ag nanoparticles

The polymer/silver composites film comprising PVP/silver nanoparticles was prepared by fixing the molar ratio of $[\text{C}=\text{O}]:\text{Ag}^+$ at 1:1. Because $\text{Al}(\text{NO}_3)_3$ was not added to the silver polymer electrolyte, the silver ions were readily converted to metallic silver nanoparticles over time. The TEM image of the as-prepared silver nanoparticles is shown in Fig. 2, revealing an average particle size of 8–15 nm. Furthermore, the silver nanoparticles were consistently monodispersed and a small amount of aggregation of the silver nanoparticles was measured. These results indicated that the amide group of PVP could stabilize the silver nanoparticles by covering the surface of the particle (see Fig. 3).

3.3. UV–vis absorption of Ag nanoparticles

The UV–vis spectra of the silver nanoparticles, shown in Fig. 4, were recorded to confirm their formation and stability. These nanoparticles were prepared from a 1:1 PVP/ AgClO_4 complex solution. The strong absorption peak at around 420 nm indicated the excitation of the surface plasmon resonance (SPR) in the silver nanoparticles. As seen in the figure, the spectrum appeared symmetric and well resolved, implying that the silver nanoparticles were monodispersed and stabilized by the PVP. Furthermore, these results indicated a more uniform size distribution in the perchlorate system, as was confirmed by TEM, where no trace of large particles was essentially found on the grids.

3.4. TGA analysis

The thermal stability was examined by performing a TGA of the electrolytes in flowing N_2 . As shown in Fig. 5, the TGA was conducted from room temperature up to 600 °C, a temperature that lies between the boiling point of the solvent and the degradation temperature of the polymer. The figure presents two distinct curves of weight loss, with and without $\text{Al}(\text{NO}_3)_3$. The first occurrence of weight loss was calculated to be about 4.5% in the range from room temperature to 350 °C and was attributed to the loss of moisture and organic solvent. The second incidence of weight loss was around 25–30% and occurred in the range of

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