Spectroelectrochemical and morphological studies of the ageing of silver nanoparticles embedded in ultra-thin perfluorinated sputter deposited films

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ARTICLE INFO

ABSTRACT

This paper focuses on the investigation of the ageing behaviour of silver nanoparticle containing polytetrafluoroethylene thin films during exposure to phosphate buffer solution (pH = 7.5). In order to investigate the effect of the electrical connection between the silver nanoparticles via a conductive substrate, two kinds of composite films were compared. One model where the nanoparticles are directly deposited on an inert conducting substrate and then covered by an ultra-thin polytetrafluoroethylene like film. In the second case a polytetrafluoroethylene/silver nanoparticle/polytetrafluoroethylene sandwich film was prepared on the same substrate to prevent electrical connection of the silver nanoparticles. Degradation was followed in-situ by means of the combination of ultraviolet–visible spectroscopy and electrochemical impedance spectroscopy. In the case of electrically connected nanoparticles electrochemical Ostwald ripening took place, while this process was not observed for the insulated nanoparticles. The electrochemical impedance spectroscopy studies allowed for the parallel study of the correlated loss of barrier properties. Transmission electron microscopy images of both composite films confirmed the results obtained by means of the in situ electrochemical ultraviolet–visible studies.

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1. Introduction

The development of antibacterial composite materials containing silver nanoparticles (AgNps) has attracted a great amount of interest in the last years due to potential applications as self-sterilizing surfaces [1–6]. AgNps are embedded in a polymer film with high barrier properties to prevent direct body contact for health and safety concerns [2,7,8]. Moreover, since the sterilizing effect is caused by the dissolution of silver ions from the AgNps, the presence of a protective polymer matrix assures a controlled release [1,3–5,7–9]. The design of high efficiency and long life time composite materials with a controlled and environment-specific silver ion release is of crucial importance. For the silver ion formation water ingress is responsible, thus the polymer layer plays an important role as the water uptake is controlled by the polymer properties [1]. The formation of silver ions from embedded particles is only possible when water penetrates the polymer and reaches the nanoparticles [1]. Damm and Münstedt investigated the ion release kinetics from nanoparticles in polyamide polymers [1]. Thus the barrier properties and the water uptake of the surrounding polymer play an important role for the release kinetics. The efficiency of the sterilizing effect and the assessment of the lifetime of the composite material can only be accomplished via a profound understanding of the release rate and behaviour of the AgNps in the polymer matrix. Self-agglomeration processes of AgNps created by sol–gel techniques on silica surfaces were analysed by X-ray photoelectron spectroscopy (XPS) by Akhavan et al. [10]. It could be demonstrated that silver particle diffusion into the porous silica takes place with an activation energy E_a ~0.08 eV due to heat treatment [10]. Thus, XPS is a useful tool to analyse the agglomeration behaviour of AgNps on surfaces. But for samples where the particles are covered by a 20 nm polytetrafluoroethylene (PTFE) top layer other techniques like X-ray Absorption Near Edge Structure (XANES) must be used to get information about the chemical state of the silver. Itami et al. showed that XANES could be used to investigate the AgNp growth in polyelectrolyte films [11]. The size dependent oxidation of AgNps on a modified indium-tin oxide (ITO) substrate was investigated by Ivanova and Zamborini [12]. By increasing the AgNp size the peak potential of the oxidation process Ag → Ag$^+$ was shifted to positive values [12]. Long term electrochemical investigation on silver containing PTFE electrodes during reduction of oxygen in alkaline solution was investigated by Wagner et al. [13]. From the results it can be concluded that electrochemical impedance spectroscopy (EIS) is a powerful tool to investigate degradation processes at such electrodes.

It has been reported that for AgNPs-loaded polymer films, Ostwald ripening may occur. Wang et al. demonstrated that changes in the nanoparticle distribution can be caused by atomic metal diffusion, coalescence between particles and electrochemical Ostwald ripening [14]. Redmond et al. studied the electrochemical Ostwald ripening of thermally evaporated silver on conductive substrates [15]. The Ostwald ripening could be controlled by the addition of an inert salt to the solution [15]. As the Ostwald ripening process may strongly affect the size distribution of the AgNps during the ageing process, resulting in a changing dissolution behaviour, the improved understanding of these processes is mandatory for the design of coatings with desired properties.

Menshykau and Compton established two different models for the study of diffusion processes through an inert layer on electrodes [16]. It is described that the electro-active species are dissolved in the layer which covers the electrode and afterwards diffusion takes place. In the second model the diffusion process proceeds via pinholes in the surrounding layer [16]. Diffusion parameters for AgNps on silica surfaces like activation energy and diffusion coefficient were calculated from atomic force microscopy measurement by Akhavan [17]. This paper focuses on the effect of connected and isolated nanoparticles during exposure to a phosphate buffer and their ageing behaviour investigated by an in situ ultraviolet–visible spectroscopy (UV/Vis), EIS cell.

Three model systems have been analysed in this work for the study of the electrical contact between AgNps and its effect on their dissolution behaviour within an ultra-thin PTFE film (Fig. 1). For the sample compartment (AgNp/PTFE), AgNps were directly deposited onto ITO coated glass substrates and coated with the PTFE-like film providing electrical contact between the AgNps. In the second model system (PTFE/AgNp/PTFE), a barrier PTFE layer was deposited between the AgNps and the ITO substrate which prevented the electrical contact between the AgNps. For comparison the pure PTFE matrix material was placed on the ITO. An in-situ combined EIS and UV/Vis technique was used to investigate dissolution of the AgNps and changes of barrier properties of the coating simultaneously [2]. Transmission electron microscopy (TEM) analysis was performed on the AgNp/PTFE and PTFE/AgNp/PTFE composite samples on carbon/copper grids (C/Cu grids) before and after ageing via exposure to electrolyte to investigate the changes occurring in the size and distribution of the AgNps.

2. Experimental

2.1. Materials and chemicals

The samples for the in situ UV/Vis EIS measurement were prepared on ITO glass (Präzisions Glas & Optik GmbH, Germany). Samples for TEM experiments were prepared on carbon-coated copper TEM grids
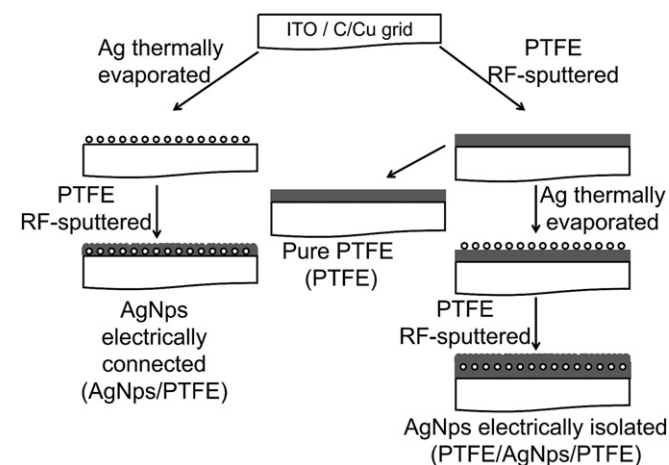
(Plano GmbH). The schematics of the three model systems under investigation are presented in Fig. 1. Nominal thickness values of the PTFE on the samples are presented in Table 1. The PTFE polymer was deposited by means of magnetron sputtering; the details of the deposition process are described elsewhere [2,18,19]. To compare the pure matrix material a sample with 20 nm PTFE was prepared on ITO. Briefly, the samples were prepared in a vacuum chamber with a base pressure of 3.4×10^{-3} mbar. The deposition rate of PTFE was set to 3.5 nm/min by means of a quartz crystal microbalance. For the PTFE, AgNp/PTFE and PTFE/AgNp/PTFE samples, the power for PTFE deposition was set to 30 W. The AgNp-layer was deposited by thermal evaporation using Ag pellets (99.99%, Goodfellow, UK).

A 0.2 M phosphate buffer containing 0.5 mM H_2O_2 resulting in a pH of 7.5 was used for the ageing experiments. The buffer was prepared with deionized water (0.055 µS/cm), $Na_2HPO_4 \cdot 7H_2O$ (Merck KGaA, analytical grade), $NaH_2PO_4 \cdot H_2O$ (Merck KGaA, analytical grade) and H_2O_2 30% (Merck KGaA, analytical grade). The pH of the buffer was determined with a pH electrode (WTW, SenTix, stored in 3 mol/l KCl). Before each experiment the buffer was freshly prepared.

TEM samples prepared on C/Cu grids were stored in the phosphate buffer solution for 5 h. After the ageing experiments the samples were rinsed carefully with deionized water (0.055 µS/cm) and afterwards carefully dried in a nitrogen stream. TEM investigations were performed using a Tecnai Supertwin F20 G2 equipped with a field emitter gun operated at 200 kV.

2.2. Analytical methods

2.2.1. EIS

EIS was performed using a Gamry Femtostat. For the EIS measurement a custom made three electrode in-situ cell was used which allows the measurement of EIS and UV/Vis at the same time. The sample was connected as a working electrode and as a counter electrode a platinum wire (Pt, Goodfellow, 99.99%) was used. An additional platinum wire served as a pseudo-reference electrode.

2.2.2. UV/Vis spectroscopy

UV/Vis investigations in the in situ EIS UV/Vis cell were performed using a UV/Vis spectrometer (Evolution 600, Thermo Scientific). For the measurement the buffer solution was filled into the cell and the UV/Vis spectra were continuously measured during the exposure.

2.2.3. EIS data fitting

Water absorption into the polymer matrix causes a change in the dielectric constant of the film, which leads to a change in the capacitance of the polymer [2,14,20,21]. The equivalent circuit in Fig. 2 was used in the data fitting for nanopores in thin films [22]. Data fitting was performed with the Gamry, EchemAnalyst software.

3. Results and discussion

3.1. EIS

In order to investigate the barrier properties of the PTFE layer during exposure to the phosphate buffer EIS has been performed. Fig. 3 shows the impedance Z_{mod} and the phase angle Z_{phz} plotted as a function of immersion time for a 20 nm PTFE coated sample and for a bare ITO substrate. The higher impedance values observed for the 20 nm PTFE coated

Fig. 1. Schematics of the sample design of Ag-PTFE nanocomposite films on ITO and C/Cu grid.

Table 1
Film thickness values of the samples prepared for the measurements.

Sample name	Total film thickness
PTFE	20 nm
AgNps/PTFE	20 nm
PTFE/AgNps/PTFE	30 nm