49th International Conference on Environmental Systems
7-11 July 2019, Boston, Massachusetts
ICES-2019-125

Mitigation of Silver Ion Loss from Solution by Polymer Coating of Metal Surfaces

John Vance[1]
KBRwyle, NASA Ames Research Center, Moffett Field, CA 94035

and

Lance Delzeit[2]
NASA Ames Research Center, Moffett Field, CA 94035

Spacecraft potable water systems require a biocidal agent that effectively provides both immediate and residual disinfection over long periods of time. Ionic silver (Ag^+) is a leading candidate for this application, but suffers from rapid concentration loss due interactions with the metal storage containers and tubing. In order to maintain biocidal efficacy in systems with long periods of dormancy and to reduce the required rate of Ag^+ injection, it is necessary to develop alternative materials and coatings for certified metal alloys that significantly reduce the Ag^+ loss. In this work, we investigate the performance of two unusual polymers, Teflon AF 2400 and parylene-AF4, as barrier coatings under immersion in 400 ppb Ag^+. We show that 25 µm-thick parylene-AF4 is a promising coating with Ag^+ losses similar to PTFE. Key challenges with this material include maintenance of adhesion under long-term immersion and control of deposition during the internal coating of high-aspect ratio tubing. Solutions to these problems may including surface structuring of substrates for mechanical anchoring or an alternative parylene-C chemistry (with more stable adhesion), and dynamic spatio-temporal control of substrate temperature, respectively.

Nomenclature

316L = Austenitic Fe-Cr-Ni-Mo stainless steel (low-carbon grade)
AdPro Plus™ = AdPro Plus proprietary adhesion promotor (Specialty Coating Systems, Inc.)
Ag^+ = Silver(I) ion
AgF = Silver(I) fluoride
A/V = Surface area/volume ratio
cm^{-1} = cm^2/cm^3
EDX = Energy-dispersive X-ray spectroscopy
HAZ = Heat-affected zone
ISE = Ion-selective electrode
ISO = International Standards Organization
LoD = Limit of detection
mL = milliliter
mm = millimeter
mV = millivolt
µm = micrometer
NaF = Sodium(I) fluoride
nm = nanometer
Parylene-AF4 = Poly(α,α,α′,α′-tetrafluoro-p-xylylene)
Parylene-C = Poly(chloro-p-xylylene)
Parylene = Poly(p-xylylene) polymers
PP = Polypropylene

---

[1] Research Engineer, Bioengineering Branch, NASA ARC N239-15, Moffett Field, CA 94035.

[2] Physical Scientist, Bioengineering Branch, NASA ARC N239-15, Moffett Field, CA 94035.

ppb = Parts per billion (mass)
ppm = Parts per million (mass)
PTFE = Polytetrafluoroethylene
rpm = rotations per minute
SCS = Specialty Coating Systems, Inc.
SEM = Scanning Electron Microscope
Teflon™ AF 2400 = Amorphous fluoroplastic (Teflon™ derivative, Chemours)
Ti-6Al-4V = Grade 5, alpha-beta titanium alloy

I: Introduction

IONIC silver, or (Ag$^+$), has been identified as a primary candidate for the disinfection of potable water systems in future human exploration missions. There is a long history concerning the use of silver for microbial inactivation, both for terrestrial applications and in spacecraft. The Russian space program has employed it on *Mir* and the International Space Station, and there has been work to replace iodine (traditionally used by NASA) with ionic silver on the U.S. segment. Ionic silver inactivates microbes through multiple mechanisms, helping to suppress deleterious biofilm formation and the spread of waterborne disease. While the biocidal efficacy of ionic silver at appropriate concentrations is well established, there is a known problem of rapid ion loss in dilute solutions, particularly to interactions at container surfaces. The depletion of Ag$^+$ over time threatens to significantly reduce biocidal activity inside potable water systems as mission duration increases and spacecraft are subject to dormancy periods of months or years. A possible solution is continual circulation and Ag$^+$ dosing to maintain biocidal levels, but this imposes system reliability and complexity issues as well as an increase in equivalent system mass, Work is ongoing on such methods, however, a complementary approach to significantly reduce Ag$^+$ adsorption by appropriate materials selection/surface modification is also necessary.

Several materials and surface treatments have been investigated for compatibility with Ag$^+$ at biocidal concentrations relevant to potable water systems. The results of these investigations have been compiled in a recent review on silver biocide for space applications by Li *et al.*[1] Significant silver loss was found in nearly all reported test materials and conditions, with the lowest qualitative loss occurring with Ag plated/Ag$^+$ treated metals/metal oxides and inert fluoropolymers. The surface area/volume ratios (A/Vs) employed in previous work vary by nearly two orders of magnitude, among other inconsistencies, making direct comparisons difficult. As higher A/Vs are found in narrow tubing, etc., the greatest risk of silver loss occurs at locations most susceptible to its negative effects. Therefore, is necessary to consider the geometry of interest when applying literature values to systems design and evaluation.

Materials substitution, including replacement of metal alloys with more inert polymers (with reported lower Ag$^+$ loss) including polytetrafluoroethylene (PTFE) appears to be a straightforward option, but the mechanical suitability of these materials in tubing, bellows, and storage vessels in deep-space potable water systems has not been demonstrated. The application of glass or ceramic materials remains generally impractical due to their lack of flexibility, formability, and mechanical resilience.

Proposed surface treatments include: passivation, electropolishing, thermal oxidation, silver plating, high-concentration Ag$^+$ preconditioning, polymer coating, and combinations of the above.[1] Passivation and electropolishing do not appear to have satisfactory performance for most metals employed in potable water systems. Silver plating on top of a thermal oxide layer appears to be suitable at low A/V conditions, but proper oxide formation depends on alloy specific processing. Oxidation also has issues with the high temperature treatment of temperature sensitive components. Silver pre-conditioning was found effective with titanium alloy at very low A/V and ineffective with a stainless steel at high A/V. High-concentration Ag$^+$ pre-conditioning appears to be of limited effectiveness in metal systems at high A/V, but may be more suitable for polymer surfaces, as electrochemical activity is greatly limited. PTFE coating was claimed effective at low A/V for a test duration of 10 months in a NASA Tech brief,[2] but it can only be deposited on relatively simple geometries with direct line-of-sight access.

The above solutions have been explored in previous work with some success, but little work has been done with conformal polymer coatings which can be deposited on the interior surfaces of components with complicated geometries and high aspect ratios. Thus, chemically inert polymer barrier coatings that could be coated onto the materials presently proven robust in potable water systems are desired. This requirement eliminated the obvious choice of PTFE, which requires spray or directional vapor deposition for high-quality films. Two potential polymer chemistries of interest were identified, amorphous Teflon AF 2400, and the vapor phase deposited parylene-AF4. Other polymer coating systems such as silicones and acrylates were ruled out for this investigation due to their chemical reactivity, coating processes, and lower barrier performance, however they may be of interest in future work.

A: Teflon AF 2400

Teflon AF 2400, unlike most fluoropolymers, is an amorphous derivative of PTFE that is soluble in a special solvent, and thus can be deposited by dip coating.[3] This provided the potential opportunity to allow the internal coating of tubing and other components with a PTFE-like coating. This made it an early candidate for this application.

However, our initial work with the material was of limited success presumably due to the extremely thin (nm-scale) thickness produced with the dilute 1% solution employed here. Dip coating with a higher concentration Teflon AF solution could be of interest in the future, but the difficulties involved with properly coating complicated internal geometries or the interior of narrow tubing may be significant.

B: Parylene-AF4

The parylene family of polymers has been developed since the middle of the last century, and a large body of work can be found in the literature examining the synthesis routes and film properties of the various chemistries. The parylenes are nearly unique in their deposition mechanism (direct vapor-phase, free-radical polymerization), which allows the conformal coating of complex internal surfaces with a wide range of obtainable film thicknesses. Deposition occurs at or near room temperature, under low vacuum, and does not require direct line of sight. Parylenes are deposited by flowing a precursor over the substrate of interest, where the precursor (an activated monomer) condenses, forming a linear polymer. The crystallinity of the resultant film depends strongly on the precursor chemistry and deposition parameters. The precursor is generally produced by “cracking” the (vapor phase) dimer form of the species of interest (the Gorham process), or by a more complicated *in situ* chemical synthesis. The deposition rate can be controlled qualitatively by controlling substrate temperature, allowing for localized control of film thickness and prevention of precursor depletion in flow-through systems. The Gorham synthesis of one of these parylenes, Parylene-AF4 (poly(α,α,α′,α′-tetrafluoro-p-xylylene)) is shown in Figure 1.[4]

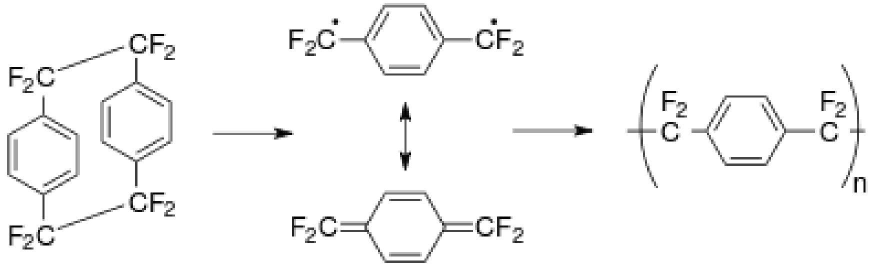

Figure 1. Schematic view of Parylene-AF4 synthesis by the Gorham process. The aliphatic fluorine results in a bridge structure analogous to PTFE.

We identified Parylene-AF4 as a strong candidate as a barrier coating to reduce the Ag^+ loss from solution. It was believed that the replacement of the aliphatic hydrogen with fluorine, parylene-AF4, would make the parylene more PTFE-like, and thus mimic the low PTFE Ag^+ loss. Additionally, the addition of the fluorine makes the parylene-AF4 more inert and resistant to temperature, UV, and other forms of radiation than the other members of the parylene family.[5] Encouragingly, a technique for internal coating of high-aspect ratio tubing with parylene-AF4 has recently been reported (using the thermal control of deposition rate mentioned previously), possibly enabling Ag^+ loss mitigation in narrow water supply lines. Parylene-AF4 was predicted to have the best overall properties and thus appropriate for a first investigation.

Beyond the need for a chemically inert surface, any polymer coating used for this application must maintain film integrity under long term water immersion. Using generic silane A-174 and proprietary AdPro Plus (Specialty Coating Systems, USA) adhesion promoters, parylene-AF4 has been deposited successfully on numerous metals and polymers. However, adhesion promotors are generally qualified for use in humid atmospheric conditions, rather than water immersion, and the longevity of sustained adhesion necessary for deep-space exploration has not been demonstrated. Possible solutions to this problem including mechanical anchoring and alternative parylene chemistry are described in the *Results and Discussion* section below.

Many of the members of the parylene family, including AF4, have been approved for implantation in human subjects by the Food and Drug Administration, with successful testing under ISO protocols.[7] This provides strong *prima facie* evidence that parylene-AF4 can be employed in spacecraft potable water systems without undue risk to astronaut health. However, further work may be required to investigate the toxicity of the leachates from these films and adhesion promoters, particularly under long-term exposures and simulated deep-space radiation. The possibility of localized metal corrosion due to film-related defects must be properly addressed. The formation of biofilms on parylene in Ag^+ depleted potable water is of obvious concern as well.

C: The Present Work

In this work, we focus on the investigation of parylene-AF4 as a barrier coating for a prototypical metal (316L stainless steel) employed in potable water systems using 400 ppb Ag^+ biocide. By preventing intimate contact with metal surfaces, we reduced the depletion of Ag^+ in solution to levels comparable to those found with PTFE. By comparative loss experiments with coated and uncoated coupons in potable water at 400 ppb Ag^+ loadings immersed for 7, 28, and 56 days, we show that inert, highly versatile parylene films are strong candidates for use as a barrier coating in potable water systems in spacecraft, and begin to address the problem of delamination.

II: Materials and Methods

A: Preliminary Experiments with Teflon AF 2400

Dip coating and curing of films on stainless steel wire followed the processing instructions of the Teflon AF 2400 solution manufacturer (Chemours). SEM imaging, EDX, and basic electrochemical testing of the barrier properties (i.e. resistivity) were measured in saline solution vs. bare metal.

B: Coupon Fabrication and Film Deposition

Coupons were cut out of cold-rolled 316L sheets (0.060" and 0.020" thickness, 2B annealed/roll-finished/passivated, thyssenkrupp OnlineMetals) and virgin PTFE 0.60" (McMaster-Carr) stock. No polishing of the coupons was done after fabrication. The immersed portion of the coupon has dimensions of approximately 0.45" x 1.8". The coupons are washed in Dawn detergent and degreased in Crystal Simple Green. All coupons were rinsed in deionized water several times after cleaning.

A quantity of each type of coupon and several flat bottom tubes were sent to Specialty Coating Systems (WI, USA) for parylene-AF4 deposition. The coupons were cleaned with an isopropanol/deionized water rinse and dried. A proprietary adhesion promoter, AdPro Plus, was applied by vapor deposition *in situ*, and then 25 μm (nominal) of parylene-AF4 was conformally deposited in a proprietary process (brand name: Parylene HT). An additional quantity of 0.060" 316L coupons were coated in-house with Teflon AF 2400 by dip coating in a 1% solution (Chemours) and curing as described in the manufacturer's instructions.

C: Coupon/film deformation

The properties of the parylene-AF4 film and metal/film interface as received from Specialty Coating Systems (SCS) and after 7-days immersion were tested qualitatively by cutting a tab in the pristine film and attempting to peel up the film. A subset of the coated coupons made from 0.020" 316L stainless steel were manually deformed by repeatedly bending 180° back-and-forth 10 times perpendicular to the coupon length (minimum radius of curvature ~5 mm) to qualitatively examine the adhesion strength of the of the films under severe deformation, fatigue, and yielding.

D: Ag^+/Water Chemistry

Concentrated stock solutions were made by dissolving 23.5 mg of AgF (99.9%, Sigma-Aldrich) and 36.5 mg of NaF (99.99%, Sigma-Aldrich) in 50 ml deionized water (Milli-Q), respectively. A potable water analogue containing 400 ppb Ag^+, 400 ppb Na^+, and 400 ppb F^- was made by adding 1 part of each stock solution to 1000 parts deionized water. The Ag^+ concentration of the potable water solution was confirmed by colorimetric analysis with a silver photometer (Hanna Instruments) and the combination ISE described below.

E: Comparative Ion Loss Experiments

Coupons were partially immersed in the Ag^+ solutions (6.0 ml) in polypropylene (PP) flat bottom tubes (12 ml, 16 mm outer diameter, Globe Scientific) (shown in Figure 2). The A/V of the immersed portion of the coupon was approximately 1.5 cm^{-1}. The coupon was suspended from a polyethylene tube cap by nylon monofilament to minimize contact with the container walls. A second tube cap was used to seal the first cap which was punctured to hang the coupon by the monofilament, thus preventing escape of water vapor or intrusion of further atmospheric oxygen into the head-space. Experiments with coated and uncoated

Figure 2. A coupon/tube set showing coupon immersion.

coupons, as described above, were done in triplicate for 7 and 28 days. Coupon/tube sets used in the 28-day experiment were then emptied and refilled with fresh Ag^+ solution for a further 28-day experiment to examine the change in Ag^+ loss after prolonged exposure. For the duration of experiment, the tube/coupon sets were stored vertically in test tube racks, at room temperature and in the dark (to prevent photoreduction of Ag^+). A subset of the various coupon/coating types were pre-conditioned with 100 ppm Ag^+ for 24 hours and then equilibrated in 400 ppb Ag^+ for 4 days prior to the loss experiments.

F: Ion Loss Determination

The concentration of silver in the bulk solution for each tube/coupon specimen was measured at the end of the exposure period using an Orion Combination Silver/Sulfide Ion Selective Electrode (ISE) (Thermo Fisher) that uses the Nernstian relationship between Ag^+ activity and electrode potential. This technique is adapted from one introduced by Durst and Duhart[8] to measure trace-level Ag^+ adsorption onto various materials, but modified by us with the use of a combination ISE rather than discrete electrodes. This allows for high-throughput, repeatable measurement of small liquid volumes inside sample tubes, at the expense of low-concentration precision. The ISE was filled with a special filling solution for low range measurements (Optimum Results C, Thermo Fisher) and calibrated with solutions of known Ag^+ concentration. No ionic strength adjuster was necessary for repeatable measurement due to the extremely low Ag^+ activity. After the test period was complete, the coupon was removed and stored separately in a dry tube. The ISE is immersed into the tube to a consistent depth, with a cross-bar magnetic spinner in the bottom of the tube operated at 200 rpm provides adequate and repeatable flow at the electrode tip. The experimental setup is shown in Figure 3. The electrode potential is allowed to settle until no change greater than 0.1 mV occurs over 30 seconds. By comparison with the concentration of silver in control tubes that did not contain coupons, the silver ion loss to the coupon surface can be measured distinctly from the loss at the polypropylene tube wall.

Figure 3. Ag^+ determination with the combination ISE in a flat-bottom tube.

III: Results and Discussion

A: Preliminary Experiments with Teflon AF 2400

SEM imaging did not find thick, uniform films with the dip coating method employed (data not shown). However, EDX results did show the presence of fluorine, thus confirming the presence of a film (data not shown). The electrochemical testing of the film did not show significant resistivity increases (data not shown), suggesting film defects and limited film thickness (est. nm scale). Teflon AF chemistries with lower curing temperatures are available in higher concentration solutions, allowing for greater film thickness (multi-μm) with dip coating. The current work did not investigate these further due to the inherent difficulty of dip coating complicated geometries without coverage defects.

B: Coupon Fabrication

The coupons of various materials were successfully coated with parylene-AF4. Unfortunately, during coupon fabrication the sheet metal was cut with a laser rather than a water jet cutter as was specified. This resulted in a heat-affected zone at the coupon edge and some deleterious effects on film adhesion and ion-loss mitigation as described below, as well as corrosion at the affected surfaces.

C: Coupon/film deformation and film delamination

It was found that prior to water immersion, the AdPro Plus adhesion promoter successfully bonded the film to the metal coupon. The strength of the film/metal interface was adequate to prevent delamination of the film by peeling. Film removal required forceful scraping with a razor blade. After deformation of the 0.020" coupons, minimal delamination was visible, while the portion of the film subject to severe strain increased in opacity, suggesting yielding and fatigue in the film. Prior to water exposure, the polymer and adhesion promoter are resilient under severe strain.

Figure 4 shows photographs of a deformed coupon after immersion, and the results of the peel test before and after immersion. In the deformed coupon, delamination was visible after a 7-day immersion period at and near the location of the bend, while ripping of the film parallel to the bending axis was occasionally visible (not shown). In the non-deformed parylene coated 316L coupons, limited delamination was visible as millimeter scale blistering. Blisters likely occurred due to gas bubble growth at surface voids or defects resulting from particulate contamination. While only limited delamination was visible in the non-deformed coupons (in the form of blisters), it was found that the adhesive strength of the film was nearly completely lost. By cutting slits into the film (Figure 4c), it was found that the film could easily be peeled off the coupon, in contradistinction to the film prior to water immersion (Figure 4b). Similar loss of adhesion was found within films exposed to water-saturated air (in the tube head-space), but not those exposed to laboratory air with less than 100% relative humidity (this effect may instead be due to wicking of water at the film/coupon interface).

We propose that the failure of adhesion at the short time-scales investigated here is driven by the deleterious interference of water at the interface of the parylene-AF4 film and the AdPro Plus, rather than at the metal-AdPro Plus interface. This is supported by a report in the literature of adhesion of parylene-C with AdPro Plus in elevated temperature phosphate-buffered saline solution for several months,[7] and our own preliminary work with parylene-C, which does not show loss of adhesion after 14-day immersion. The different chemistry (non-fluorinated) of parylene-C may allow long-term adhesion at room temperature and might be a more suitable film material, as we have found it has a similarly low Ag^+ loss to the film surface in early-stage tests. Moderate-temperature annealing to improve the crystallinity and adhesion of parylene-C would help to reduce water vapor diffusion and subsequent loss of adhesion, if the required temperature of ~ 125-150° C does not damage the AdPro Plus adhesion promotor, as was claimed to occur with 200° C annealing in Reference 7.

Although there is limited prospect for improving the performance of chemical adhesion promotors with parylene-AF4, due the material's weakly interacting fluorine substituents, an alternative mechanism of adhesion can be supported by the production of surface nanostructure on the metal. This allows for mechanical anchoring of the film to the metal and adhesion based on the cohesive strength of the parylene film, which is much less severely affected by water immersion. Such a technique has been successfully demonstrated for the anchoring of parylene-C to titanium alloys.[10] Figure 5 shows a sodium metatitanate nanostructure produced on a titanium alloy (Ti-6Al-4V) coupon. It was produced by an ambient pressure hydrothermal process in concentrated NaOH solution at 60° C, following the procedures reported in Reference 10. Similar surface modifications for mechanical anchoring may be possible on other alloys, including stainless steels, and we are investigating them presently.

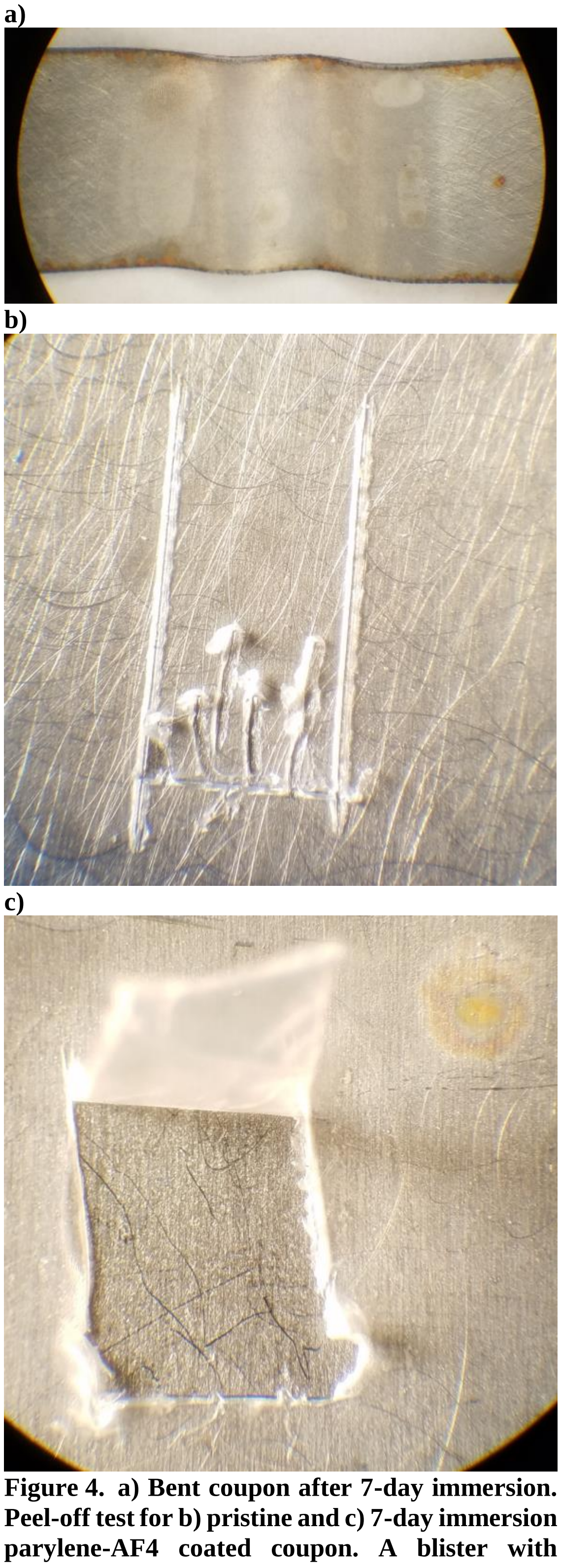

Figure 4. a) Bent coupon after 7-day immersion. Peel-off test for b) pristine and c) 7-day immersion parylene-AF4 coated coupon. A blister with localized surface discoloration is visible in c).

While the severe reduction of adhesion strength on smooth metal substrates poses a problem for long-term reliability, it may be possible to reduce or eliminate subsequent delamination. Blistering might be reduced by electropolishing the metal surface to eliminate surface defects larger than the critical size for gas bubble driven delamination or by more careful surface cleaning. Stress driven delamination can be prevented by requiring film deposition to be done after any bending or other material forming operations. Protection of film edges may be key to preventing undercutting and film lift-off due to water interpenetration.

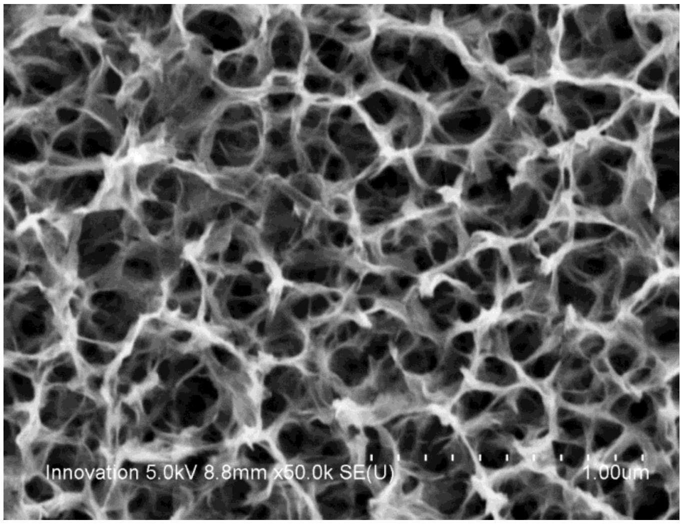

Figure 5. Surface nanostructuring on Ti-6Al-4V for mechanical film anchoring.

D: Ag$^+$/Water Chemistry

The solutions were prepared as described above.

E: Comparative Ion Loss Experiments

The results of the comparative ion loss experiments are shown in Table 1 and in a subset of the results in chart form in Figure 6. The table provides granular results at the individual coupon level to help discriminate silver loss due to the film vs. adsorption on the metal coupon resulting from partial delamination. Delamination is evident by the increased Ag$^+$ loss vs. the other coupons of a similar type, as well as by visible corrosion at the edges of the coupon (data not shown). These effects resulted in worse performance than would be observed with coupons cut by water jet (data not shown), and laser cutting is clearly not appropriate for this application.

The parylene-AF4 coated tubes without coupons had approximately zero loss vs. the polypropylene control tubes after a 28-day exposure, and after refilling and conducting a further 28-day exposure. These results suggest that the parylene-AF4 film itself has very low Ag$^+$ loss, similar to polypropylene. The parylene-AF4 coated coupons (0.060") had mean losses of 5% (7-day) and 21% (28-day). By inspecting the individual coupon data at 28-days, we see that delamination in one coupon increased the mean significantly from the ~ 10% loss/28-day immersion for coupons without significant delamination. This is supported by investigating the further 28-day immersion of these same coupons (mean 39% loss). We expect decreased loss after refilling and further exposure due to saturation of the polymer surface. The increased delamination and exposure of bare metal counteracts this expected decrease in the Ag$^+$ loss. The results of the parylene-AF4 coated coupons (0.020") support this assumption, with mean losses of 6% (7-day) and 12% (28-day). The approximate loss of ~10%/28-days at an A/V of 1.5 cm^{-1} shows qualitatively similar performance to PTFE as reported in Reference 11 (~ 65% loss at A/V of = 5 cm^{-1}, 30° C, 28-day exposure), given the more demanding geometry employed in that experiment.

The bent, parylene-AF4 coated 0.020" thick 316L coupons were observed to have mean losses of 33% and 79% (Table 1), respectively, showing that strain related delamination can cause significant loss even if the area fraction of delaminated film is relatively small. Uncoated 316L coupons and Teflon AF 2400 coated coupons lost nearly all Ag$^+$ (>90%), near or below LoD in the 7-day experiments. Bare 316L coupons pre-treated with 100 ppm Ag$^+$ did not show significant improvement in performance. The failure of Teflon AF 2400 to significantly mitigate Ag$^+$ loss suggests that thin (nm scale) films with incomplete coverage are not useful for this application. The bare and parylene-AF4 coated PTFE coupons had mean losses of 8% and 5% (7-day), and 16% and 1%* (28-day), respectively (*this result may be speciously low).

The 100 ppm Ag$^+$ pre-treated bare and parylene-AF4coated PTFE coupons had mean Ag$^+$ losses of -1% and 8% (7-day) and 0% and -2% (28-day) for the bare and coated set, respectively. The data here is inconclusive, but suggests high-concentration pre-conditioning (or extrapolating, long-duration higher-level exposure) of parylene and PTFE surfaces may result in very low to nil loss; further experimentation is clearly necessary, along with an appropriate cleaning method for the slightly porous PTFE stock employed here. The results of pre-treatment of parylene-AF4 coated 316L coupons on loss were inconclusive due to the occasional increased delamination resulting from longer immersion time, and again, more work is required on this question.

Table 1. Full results of comparative ion loss experiments.

Sample type:	**Percent loss vs. polypropylene control tube [%]**					
	7-day			**28-day**		
	Individual measurements	**Mean**	**Std. dev.**	**Individuals**	**Mean**	**Std. dev.**
AF4/PP tube/28-day	no experiment			-6, 2, 5	0	5
AF4/PP tube/repeat	no experiment			-3, -2, 2	-1	2
AF4/316L:0.060"	7, 4, 3	5	2	7, 44, 12	21	17
AF4/316L:0.060"/repeat	no experiment			19, 61, 38	39	17
AF4/316L:0.060"/Ag^+	8, -5, 41	15	19	0, 25, 1	9	12
AF4/316L:0.020"	7, 6, 5	6	1	6, 23, 7	12	8
AF4/316L:0.020'/bent	32, 34, 34,	33	1	82, 76, 77	79	3
Bare/316L:0.060"	>90 for all			>90 for all		
Bare/316L:0.060"/Ag^+	>90 for all			>80 for all		
AF 2400/316L:0.060"	>90 for all			>90 for all		
AF4/PTFE	6, 6, 4	5	1	8, -3, -2	1	5
AF4/PTFE/Ag^+	10, 14, 1	8	5	-1, -4, -2	-2	1
Bare/PTFE	8, 7, 7	8	0.5	12, 21, 15	16	4
Bare/PTFE/Ag^+	0, 0, -3	-1	1	2, 0, -1	0	1

Sample legend: ***Coating type/Substrate type/Additional notes***

28-day: specimens for 28-day exposure
316L: stainless steel coupon
AF4: 25 μm parylene-AF4 coating over substrate
AF 2400: nm thickness of AF 2400 over substrate
Ag^+: Pre-treatment with 100 ppm Ag^+ for 24 h, followed by 400 ppb Ag^+ for 4 days
Bent: Coupons bent prior to Ag^+ exposure as described in *Materials and Methods* section
PP tube: PP tube with no coupon, coating on tube
PTFE: PTFE coupon
Repeat: 28-day specimens refilled with fresh Ag^+ solution and exposed for further 28 days

F: Ion Loss Determination

The combination silver sulfide ISE proved a useful tool for characterizing ion-loss. We observed significant deviation from the ideal Nernst slope of 59 mV/decade at concentrations below 100 ppb, suggesting that the combination ISE is less suited to very-low level measurements than a potentiometric cell with discrete ISE and double-junction reference electrode. Since the higher Ag^+ concentration values were of greater interest, i.e., low Ag^+ loss of coated coupons, the lowest concertation data points (20 and 40 ppb) were excluded when finding the Nernst slope for percentage loss calculations. This prevented underestimation of the Ag^+ loss near 400 ppb (typical slopes were 50-55 mV/decade). The LoD was generally ~20 - 40 ppb Ag^+, corresponding to 90-95% loss. To prevent excessive measurement drift, it was important to minimize the slight leakage of (Ag^+ containing) electrode fill solution at the liquid junction of the combination ISE/reference electrode. This was done by manually compressing the porous liquid junction seal, limiting the stir-bar speed, and maintaining the filling solution level just above the inner reference electrode junction to reduce pressure head.

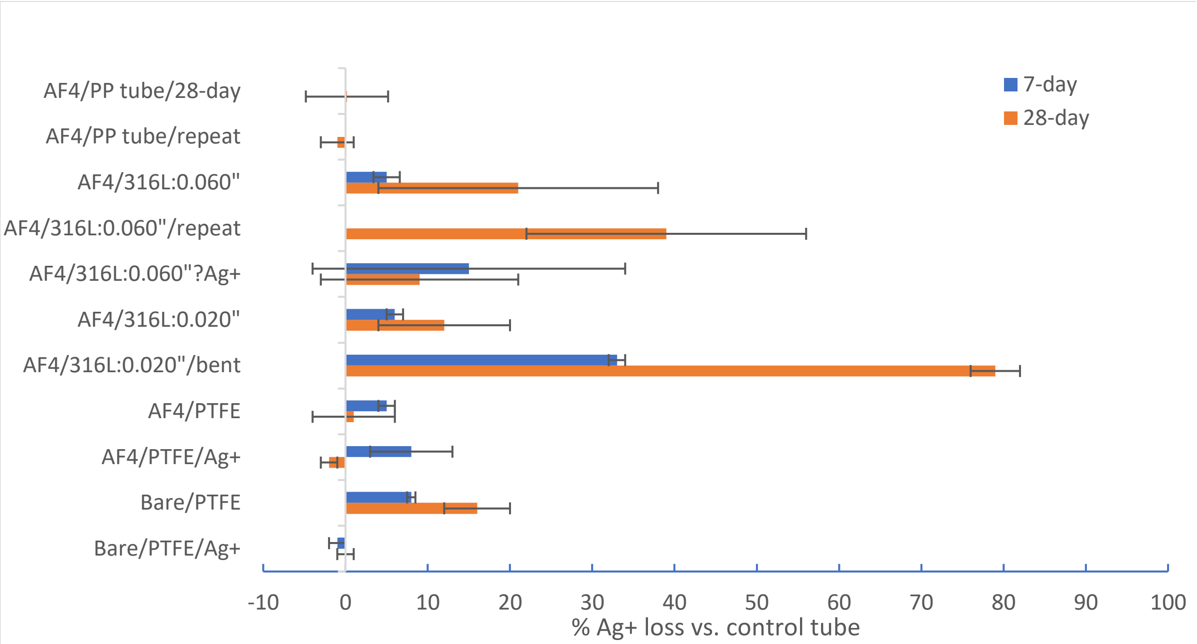

Figure 6. Selected results of comparative ion loss experiments.

IV: Conclusions and Future Work

In this work, we have reported the novel application of two conformal polymer coatings, Teflon AF 2400 and parylene-AF4, to the mitigation of Ag^+ loss at biocidal concentrations. The low concentration solutions of Teflon AF 2400 employed were found to produce films that were ineffective to be of use when dip coated, but higher concentration solutions are available and may be of future interest. With parylene-AF4, we have shown significant reduction in the Ag^+ loss on coated 316L stainless steel coupons (comparable to PTFE) with sample exposures of up to 8 weeks and an A/V of ~ 1.5 cm^{-1}. The parylene family of polymers offers a promising means of maintaining effective biocidal concentrations of Ag^+ in potable water systems built with metal components. Important issues that must be addressed include prevention of film delamination and the further development of deposition techniques and apparatus for high aspect ratio tubing. To prevent excessive loss in high A/V geometries such as tubing, pre-treatment with concentrated Ag^+ to possibly reduce adsorption rates must be investigated and demonstrated. If these can be solved, it may be possible to build potable water storage and plumbing systems with a range of currently certified alloys while avoiding the near total loss of biocidal Ag^+ after only days or weeks. The versatility of the room-temperature, conformal vapor deposition process allows the substrate-independent coating of components ranging from narrow diameter supply tubing to deformable metal bellows.

Future work will investigate the application of parylene-AF4 and parylene-C and silver ion loss inside stainless steel tube/Swagelok™ fitting systems. In addition, the long-term delamination resistance of parylene-C will be tested. High-concentration Ag^+ preconditioning and the use of surface structure modification for mechanical anchoring will be explored. If the basic problems of adhesion can be solved, an extreme test of the reliability of parylene films will be on metal bellows tanks, which would subject the film to severe and repetitive localized deformation.

Acknowledgments

The authors would like to thank Steve Gierish of Specialty Coating Systems for his assistance with the parylene deposition and John Hogan for supplying deionized water. We also acknowledge the AES Life Support System Project for financial support.

References

[1] Li, W., Calle, L., Handford, A., Stambaugh, I., and Callahan, M., "Investigation of Silver Biocide as a Disinfection Tehcnology for Spacecraft – An Early Literature Review," *48th International Conference on Environmental Systems*, ICES-2018, 8-12 July 2018, Albuquerque, New Mexico.

[2] Steele, J., Beringer, D., and Nalette, T., "Method for Reduction of Silver Biocide Plating on Metal Surfaces," *NASA Tech Briefs*, July 2013, p. 9.

[3] "Teflon™ AF Solutions," 2017, The Chemours Co. FC, LLC, 28 Feb. 2019 <https://www.chemours.com/Teflon_Industrial/en_US/assets/downloads/teflon-af-solutions-product-information.pdf>

[4] W. R. Dolbier Jr. and W. F. Beach, "Parylene-AF4: a polymer with exceptional dielectric and thermal properties," *Journal of Fluorine Chemistry*, vol. 122, no. 1, 2003, pp. 97–104.

[5] "SCS Parylene Properties," 2016, Specialty Coating Systems, Inc., 28 Feb. 2019 <https://scscoatings.com/wp-content/uploads/2017/09/02-SCS-Parylene-Properties-1016.pdf>

[6] Desai, C. and Laube, N., "Development of a technical approach to modify the internal surface of biomedical tubes and other elongated small lumen macrodevices with parylene coating," *Journal of Coatings Technology and Research*, vol. 16, no. 1, 2019, pp. 103-111.

[7] "SCS Medical Coatings," 2016, Specialty Coating Systems, Inc., 28 Feb. 2019 <https://scscoatings.com/wp-content/uploads/2015/09/SCSMedicalCoatings0116.pdf>

[8] Durst, R., and Duhart, B. "Ion-Selective Electrode Study of Trace Silver Ion Adsorption on Selected Surfaces," *Analytical Chemistry*, vol. 42, no. 9, 1970.

[9] Ortigoza-Diaz, J., Scholten, K., and Meng, E., "Characterization and Modification of Adhesion in Dry and Wet Environments in Thin-Film Parylene Systems," *Journal of Microelectromechanical Systems*, vol. 27, no. 5, 2018.

[10] Staufert, S., Gutzwiller, P., Mushtaq, F., and Hierold, C., "Surface Nanostructuring of Ti6Al4 V Surfaces for Parylene-C Coatings with Ultradurable Adhesion," *ACS Applied Nano Materials*, vol. 1, no. 4, 2018.

[11] Petala, M., Tsiridis, V., Darakas, E., Mintsouli, I., Sotiropoulos, S., Kostoglou, M., Karapantsios, T., and Rebeyre, P., "Silver Deposition on Wetted Materials Used in the Potable Water Systems of the International Space Station," *46th International Conference on Environmental Systems*, ICES-2016, 10-14 July 2016, Vienna, Austria.