알루미늄 합금 위에 전착된 폴리피롤/폴리스티렌설포네이트 필름들의 형상변화와 표면전기전도도 조절을 위한 PSS와 산성화 이온 농도의 영향

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Effect of PSS and Acidified Ion Concentrations for Morphological and Electrical Control of Ppy-PSS Films Electrodeposited on Al Alloy

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초록: 피롤 단량체는 균일하고 접착력 있는 폴리피롤 고분자로 알루미늄 합금 전극 위에 성공적으로 전착되었다. 다양한 농도의 질산으로 산성화된 전해질 용액 안에서 전하보상 상대이온이면서 메트릭스의 역할을 하는 폴리스티렌설포네이트 고분자를 첨가하면 첨가량에 따라 폴리피롤 고분자의 표면 모폴로지와 전기적 특성이 변화됨을 보고한다. 일정한 전하 밀도(1 mAcm^{-2})에서 수행된 전압-시간 중합 곡선은 폴리피롤이 초기 핵 생성 단계에서 2차원적인 성장으로 전이하는 전압 거동을 나타내었다. SEM-EDS 분석을 이용한 이 필름들의 특성은 전압-시간 곡선에서 예상되었던 것과 같이 폴리피롤의 성장 메커니즘과 일치함을 보였다. 더 나아가, C-AFM 관찰을 통해 Al alloy 위에 형성된 폴리피롤 고분자막의 전류 이미지와 모폴로지가 질산 산성화 농도와 피롤을 포함한 PSS의 첨가 농도에 의존하여 변화됨을 서술할 것이다.

Abstract: Homogeneous and adherent polypyrrole (Ppy) coatings were successfully obtained on Al alloy electrodes in various nitric acidified solutions with pyrrole (Py) monomers. Surface morphological and electrical properties of Ppy coating were controlled by the amount of additional anion polystyrenesulfonate (PSS), which played roles of matrix and charge compensating counterion. The potential-time curves were characterized by transition potential behavior from the initial nucleation step to the two-dimensional lateral growth step under constant potential and all the electrochemical processes were conducted under a constant charge density of 1 mAcm^{-2}. The characterization of these films by scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) was consistent with the growth mechanism of Ppy as expected from the potential-time curve. Further, though C-AFM analysis, the morphological and current images of Ppy-PSS films on Al alloy were influenced according to various experimental parameters such as different acidified nitric acid and PSS concentrations containing Py.

Keywords: polypyrrole, polystyrenesulfonate, aluminum alloy, electrodeposition.

Introduction

Conducting polymers are typically prepared by chemical and electrochemical methods. The electronic properties of polymer films deposited on active or (more typically) noble metal surfaces can be reversibly altered by chemical and electrochemical doping; thus these polymer films act as insulators or conductors depending on the doping process. The direct Ppy electrodeposition on Al or Al alloys in H_2SO_4 solution via electron transfer mediation have been studied since a polypyrrole (Ppy)/Tiron film shows better adhesion to the substrate than do common electrically conducting polymers (ECPs).[1-4]

This paper presents the method of electrodeposition of a Ppy/polyanion system on an Al alloy; here polystyrenesulfonate (PSS) is used as the polyanion system. Yang *et al.* used a polyaniline (PANI)/polyanion system to synthesize a molecular complex of a double-stranded polymer resembling a DNA

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structure.[5-7] According to Yang, the synthetic process involves the absorption of the aniline monomer on polyanion chain and subsequent formation of the polymeric complex via polymerization of the adsorbed aniline. The polyanion essentially functions as a template and supports the growth of PANI.

In contrast to PANI, Ppy does not form a double-stranded structure in the presence of PSS; this is because the aniline ring becomes positively charged during the polymerization process, while the pyrrole (Py) ring does not. Thus, PSS-doped Ppy can be used to form cationic ion exchange films in the form of micellar aggregates, which contain a number of SO_3^- groups from the PSS anion. The aggregates facilitate the interaction of Py with defect sites on the oxide surface as have been explained in our previous report.[4]

The Ppy/PSS cationic ion exchange film has three distinct advantages over conventional ion exchange films when used for corrosion protection; (i) the conductive state of the polymer is highly stable because the polymeric dopant is trapped within the stable complex; (ii) SO_3^- group of the polymeric dopant enhances adhesion between the metal and the topcoat; (iii) the conducting polymer prevents the progressive invasion of chloride anion because of PSS.

The use of PSS as a polyanion system has also been demonstrated by Yang et al., who successfully prevented corrosion of the Al alloy substrate in the chemical synthesis of PANI using PSS. Recently, Ppy has been electrodeposited in a duplex (or bilayer) structure to obtain a Ppy oxalate/PSS films, on iron substrate.[8,9]

Naoi et al. reported that Ppy doped with surfactant sulfonate electrolytes such as sodium n-dodecylbenzenesulfonate readily form films on Al substrates. However, PSS doped Ppy show poor film formation ability on an Al electrode.[10] The main cause of the failure of Ppy deposition is probably the inadequate transport of PSS, which is a large polymeric anion in the compact and thick barrier-type Al oxide layer.

The electrolyte anion significantly influences the type of oxide that develops on the Al substrate. HNO_3, H_2SO_4, and $H_2C_2O_4$ (oxalic acid) are the most common aqueous electrolytes used for the electrodeposition of Ppy on Al.[11] The electro-chemical behavior of Al in an aqueous electrolyte such as HNO_3 is characterized by the presence of an Al_2O_3 layer with anodic pits. The diameter of the pits using aqueous HNO_3 is approximately 30 μm, which is three times that of the pits formed in the duplex structure grown using H_2SO_4 and $H_2C_2O_4$ as the electrolyte.[11]

HNO_3 was chosen as the electrolyte for forming the structure of the oxide layer of Al alloy of pitted type so as to enable the transport of the monomer and dopant inside this layer; this enabled the incorporation of PSS into the oxide film during the electrodeposition of Ppy on Al alloy.

This paper reports the results of the direct galvanostatic electrodeposition of Ppy-PSS films on AA 2024-T3 alloy using a various concentration solutions of PSS and acidified HNO_3 containing 0.1 M Py monomer. I also describe the growth mechanism of the Ppy-PSS film on the AA 2024-T3 alloy and report the effects of thickness, morphology and conductivity of Ppy film electrodeposited in various concentrations of PSS and acidified HNO_3.

Experimental

Aluminum alloy (AA 2024-T3) panels of dimension 5 by 8 inches was supplied by Q-Panel of Cleveland, OH. Py monomer, PSS (M_w=70000) and nitric acid (60% assay) were purchased from Aldrich Co. of St. Louis, MO. The Py was freshly distilled before use and the nitric acid was used as received. Other acids were obtained from Aldrich Co. and were used as received. Waters (18 MΩ cm conductivity) used in the experiment was obtained using a Milli-Q system supplied by Millipore Corp.

Galvanostatic electrodeposition of Ppy was performed in a one-compartment, 150 mL, three electrode cell which included the AA 2024-T3 alloy as the working electrode, a 20 cm^2 platinum plate counter electrode, and a saturated calomel reference electrode. The working and counter electrodes were arranged parallel to each another to facilitate uniform current distribution. Working electrodes of 4 cm×5 cm were sectioned from the AA2024-T3 alloy panels and the surfaces were prepared by polishing with 600 grit silicon carbide sandpaper followed by degreasing with a hexane wash and air-dried. Current densities and passed charges for the electrodeposition of all Ppy films were 1 mA/cm^2 and 1 C/cm^2 (front side deposit only), respectively. The pH of the solution containing Py and and PSS was about 1.65 in 0.015 M nitric acid, 1.00 in 0.1M nitric acid, measured using a digital pH meter 125 from Corning. The Ppy films were electrodeposited using an EG&G Princeton Applied Research potentiostat/galvanostat model 273A.

Surface morphology and analysis of the electrodeposited Ppy films were carried out using a JEOL JSM-6300 SEM (JEOL USA, Inc., Peabody, Massachusetts) equipped with Noran Vantage energy dispersive X-ray (EDS) analyzer that included a digital pulse processor with a SiLi 10 mm^2 crystal.

SEM images were taken at 15 kV with different spectral resolution ranges. Samples were mounted on aluminum mounts and viewed uncoated.

The film thickness was measured using an Elcometer 345 thickness tester for non-ferrous coatings on metal by average estimates of 4 times in the other position and the cross-sectional view of the SEM image.

Contact mode atomic force microscopy (AFM) was performed using a conductive module, so-called conductive(C)-AFM mode working in topping with Nanoscope IIIa from Extender electronics module (supplied by Dimension 3100; Veeco Instruments, USA). C-AFM using the Pt/Ir coated cantilevers was used to simultaneously obtain topographical and current images. The DC bias voltage between the substrate (Al alloy, AA2024-T3) and conducting cantilever, which was grounded, was 100 mV during all the imaging experiments. All images were obtained in air under ambient conditions and collected over a scan range of 20 μm. C-AFM measurements of the all Ppy films were performed on 1 cm^2 samples.

Results and Discussion

It is suggested in this work that the PSS polymeric anion would be more accessible to the AA 2024-T3 substrate due to the large pore sizes associated with the pitted anodic oxide structure formed with nitric acid as compared to the duplex anodic oxide structure associated with H_2SO_4 and $H_2C_2O_4$ acids.[11] In other words, growth of pitted AA 2024 alloy oxide with micron-meter size crack of the Al_2O_3 layer started to Al surface can play an important role as provide conducting paths like Al case (process 1).[11] Nucleation formation of Ppy-PSS film can be globally started over ensemble surface growth of film because Py monomer and PSS as polymeric dopant freely accessible inside conducting paths through Al_2O_3 pitted layer that modified by nitric acid (process 2). In the presence of pyrrole, these pores are filled with electrodeposited Ppy and are totally inhibited the anodic corrosion of the Al metal.

The following described experiments were designed to address this suggestion. An experiment was conducted where Ppy was electrodeposited in nitric acid solution containing PSS.

Potential/time curves for the galvanostatic deposition of Ppy at a current density of 1 mA/cm^2 on AA 2024-T3 depended on different PSS concentration is shown in Figure 1. Each curve can be divided to potential region of four step as marked on curves. The open circuit potential, V_{oc} was recorded for 20 sec
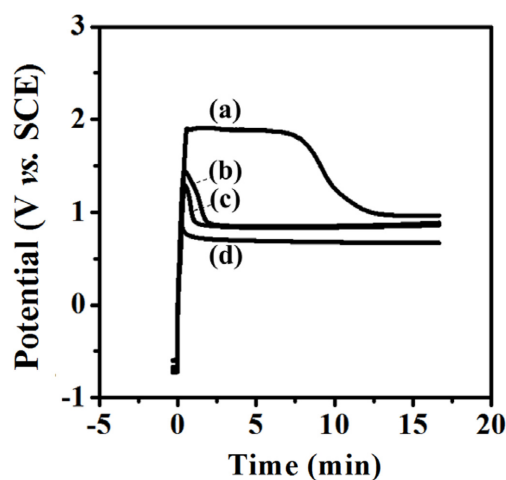

Figure 1. Potential profiles during galvanic deposition(1 mA/cm^2) of Ppy-PSS on AA 2024-T3 in 0.1 M Py + different PSS concentration acidified with nitric acid (pH=1.65): (a) 0.1 M Py + no PSS + acidified HNO_3; (b) 0.1 M Py + 0.1 mM PSS + acidified HNO_3; (c) 0.1 M Py + 1 mM PSS + acidified HNO_3; (d) 0.1 M Py + 0.1 M PSS + acidified HNO_3.

prior to application of the current (at time zero) in solution containing the monomer, PSS in nitric acid (pH=1.65). In regardless of concentration of PSS, the initial V_{oc} was approximately -0.75 V (vs. SCE), whereas in the present of 0.05 M Tiron was -0.6 V and 0.05 M Na-pTS was -1.0 V (vs. sat. Ag/AgCl). When a current of 1 mA/cm^2 was then applied between the reference and Al alloy working electrode, the potential was rapidly increased toward Ppy nucleation potential between 1 and 2 V (vs. SCE). With no PSS present the nucleation potential of Ppy increased by nearly 1.9 V within 30 sec. With PSS present, as the PSS concentration increases, that potential shifted to lower potential within 20 sec. As the PSS concentration increases, PSS participation results in the faster growth transition behavior and lower nucleation potential than without PSS condition. For nitric acid only condition with no PSS present, the rather high nucleation potential (maximum potential in the transient) and the slow transition of nucleation to growth are indicated formation of insulating polymer or impediment of nucleation at the oxide surface. These observations support that the PSS facilitate nucleation and 2-dimensional growth reaction of Ppy on the AA 2024-T3.

To demonstrate the AA2024-T3/Ppy formation, the transitions of the surface morphology were observed by SEM-EDS in all same condition of the applied current density of 1 mA/cm^2 ($Q = 1$ C/cm^2) with a different PSS concentration in Figure 2. If we compare a result of no PSS and that of 0.1 mM PSS, we can observe a lot of Ppy nuclei of 2 μm of diameter
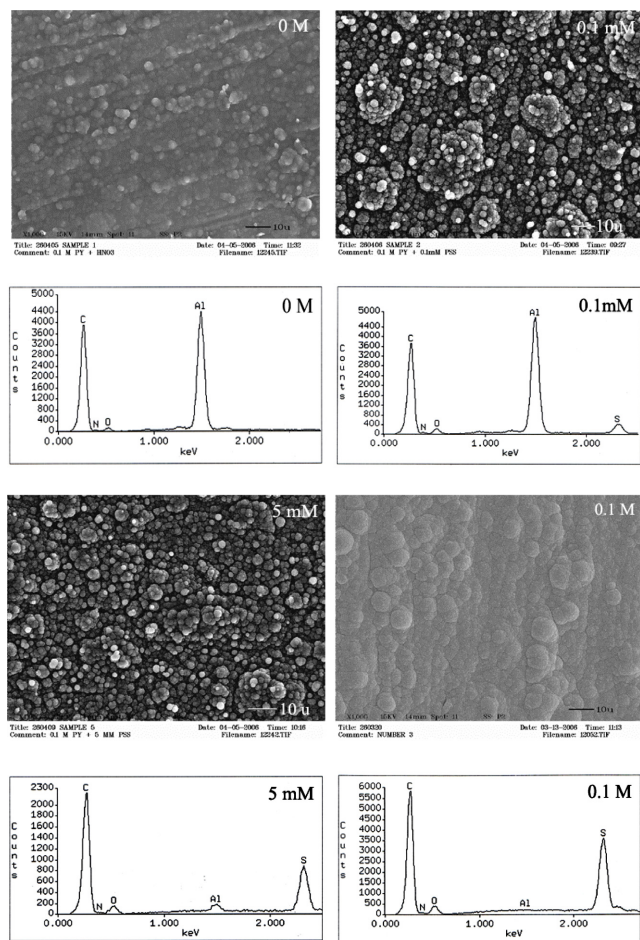
Figure 2. SEM & EDS of electrodeposited films on AA2024-T3 alloy in 0.1 M Py + different PSS concentration (0, 0.1 mM, 5 mM, and 0.1 M PSS) with acidified nitric acid solution (pH=1.65).

and few islands of 10-20 μm of diameter on the AA2024-T3 oxide layer. This phenomenon is related to show far lower nucleation potential in 0.1 mM PSS than that in no PSS. The

fact demonstrates that the PSS in these concentrations can contribute to the creation of rather Ppy nuclei and then simultaneous increase in the number of Ppy nuclei even though in presence of quite small amount of PSS. Following EDS analysis result is very well consistent with these phenomena. The ratio of the integrated EDS peaks between aluminum and carbon is shown in Figure 3(a). The Al peak intensity was higher than that of the carbon peak in 0.1 mM PSS, but started to decrease for concentrations exceeding 1.6 mM PSS. The Al peak remained quite small in 5 mM PSS and completely disappeared in 0.1 M PSS concentration. PSS incorporation in the 5 mM PSS concentration facilitated lateral direction growth prior to the vertical direction growth on Al alloy substrate. A Ppy film in 0.1 M PSS concentration was completely covered on the AA 2024 alloy surface. The sulfur (S) peak intensity was higher than that of the Al peak in 5 mM PSS and started to gradually increase from exceeding 0.1 mM PSS concentrations. A Ppy film in 0.1 M PSS concentration was composed mainly of carbon and sulfur peak, and low intensity oxygen peak. Martins *et al.* reported in their recent results that the similar transitions of surface morphology of Ppy films were observed when secondary and backscattering electrons applied to constant current of 3 mA/cm². It is possible to say that morphological alteration and potential transition between initial nucleation potential and constant growth potential depend on surface reactivity on competitive vertical growth of independent nuclei as well as on lateral growth between cross-linked nuclei.[12] The ratio of the integrated EDS peaks between sulfur and carbon is shown in Figure 3(b). The sulfur S peak increased as the carbon C peak increased. This result demonstrated that sulfur was broadly inserted during both the vertical and 2-demensional lateral growth on Al alloy substrate.
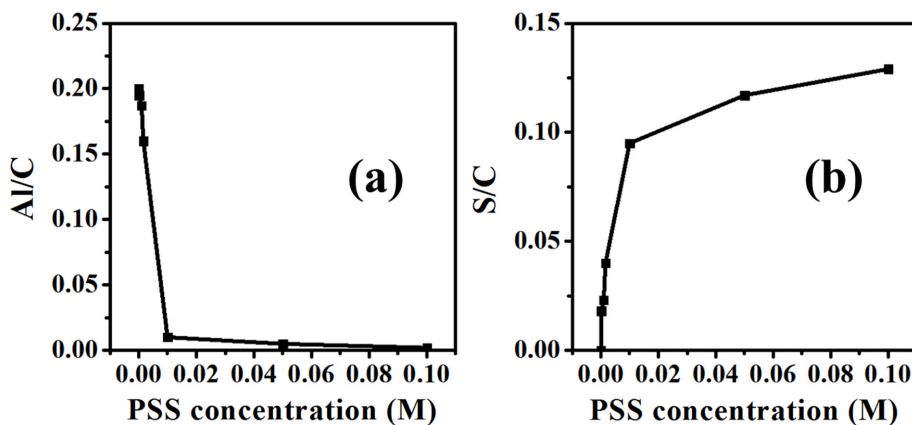

Figure 3. Elemental ratio profiles of electrodeposited films obtained from Figure 2: (a) aluminum/carbon; (b) sulfur/carbon.
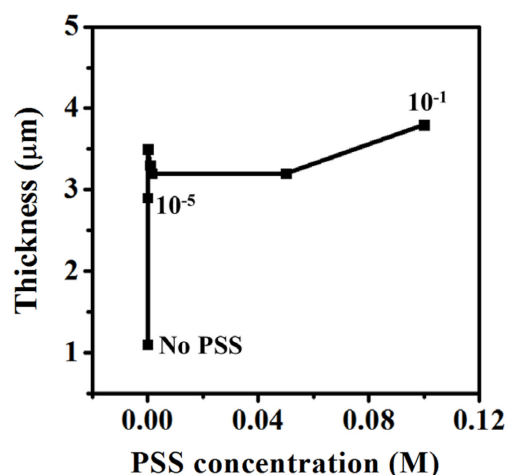
Figure 4. Film thicknesses electrodeposited on AA2024-T3 alloy in 0.1 M Py and different PSS concentrations acidified with nitric acid (pH=1.65).

The thickness of films electrodeposited on AA2024-T3 alloy in 0.1 M Py with different concentrations of acidified with nitric acid (pH =1.65) is shown in Figure 4. The average thicknesses of films were ranged from 1 to 1.5 μm when PSS was

not included and jumped up to 3 to 4 μm when PSS was included (pH=1.65). This result meant that even small amounts of PSS in the electrolyte play a role in facilitating the growth rate of Ppy. Even though the PSS addition amount altered broad range between 0.1 mM and 0.1 M, the Ppy films showed quite similar thickness values.

Figure 5 was shown the typical topographical images (1st row), current images (2nd row), and cross-sectional current profiles (3rd row). Approximate conductivities of every sample were compared with electrodeposited different condition Ppy films such as alteration of pH, acidified nitric acid, with and without PSS (or pTS) addition. The polymer surface contained a number of spots between 100 and 200 nm on a few micro-size globular structure in the topographic image that was consistent with results as observed with SEM. Film synthesized in 0.1 M Ppy with 0.015 M HNO_3 (1C) with no PSS exhibited low localized currents of picoampere (pA) with an average value of 0.015 pA. The results demonstrated that nitric acid is very little dopant, so polymer can't occur oxidation reaction. However, Ppy films with PSS exhibited larger currents of the nanoampere (nA) scale, averaging 4.77 nA for 0.1 M PSS and
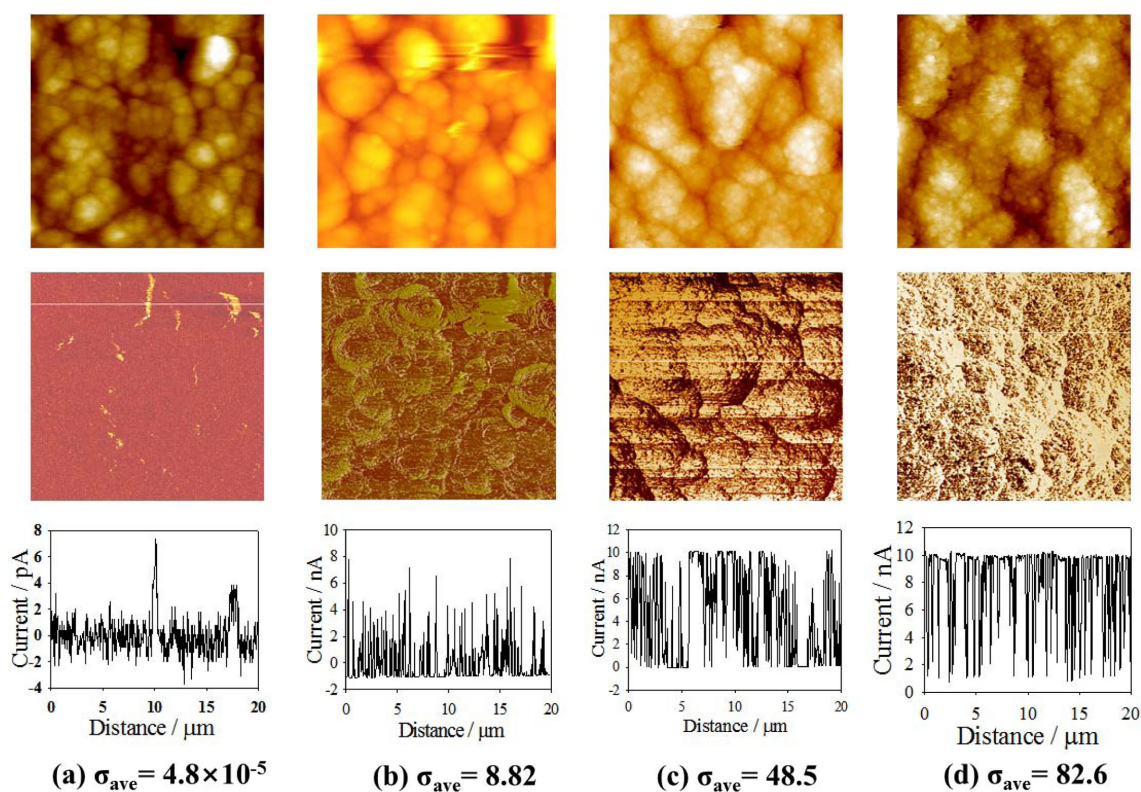

Figure 5. Effect of PSS and acidified ion concentrations for topography and average surface conductivity control of Ppy-PSS films deposited with an applied charge of 1C: (a) 0.1 M Py + 0.015 M HNO_3 (pH=1.65); (b) 0.1 M Py + 0.1M pTS + 0.1 M HNO_3 (pH=1); (c) 0.1 M Py + 0.1M PSS + 0.015 M HNO_3 (pH=1.65); (d) 0.1 M Py + 0.1M PSS + 0.1 M HNO_3 (pH=1); conductivity (σ) unit, S/cm.

a pH of 1.65. The current map of Ppy films with 0.1 M PSS with pH 1.0 showed a rather uniform current flow over the entire surface area from the substrate to the tip through the Ppy film with an average current of 8.13 nA. Average currents of films formed with PSS were at least 3 orders greater than those of films formed without PSS. On the other hand, in films synthesized with different nitric acid containing monomer and 0.1 M PSS, the average conductivity value (σ_{ave}) of film increased with the increase of nitric acid concentration. The σ_{ave} of films formed with PSS were at least 5 orders of magnitude larger than films formed without PSS. The conductivity (σ) was calculated using the equation:

$$\sigma \ (S/cm) = 1/R \times L/A$$

where L is the film thickness and A is contact area between the tip and sample. The average thicknesses of the three films were 1.2 μm (±55.5 nm) for with no PSS, 3.8 μm (±155.7 nm) and 3.6 μm (±135.6 nm) for with PSS (pH=1.65), and with PSS (pH=1), respectively. The average conductivity values obtained from the cross-sectional analyses of the current images in Figure 5 are 4.8×10^{-5}, 8.82, 48.5, 82.6 for no PSS, pTS, PSS (pH 1.65), and PSS (pH 1.0), respectively, when applied the bias voltage of 100 mV and calculated to be 37.4 nm^2 assuming the Poisson's ratio of Ppy was 0.38 just as for platinum and Young's modulus of all Ppy films was 1.1 GPa similar to that of pTS-doped Ppy.[13,14] The route mean square roughness (R_{rms}) of samples were 183.47, 244.27, 473.33 nm for 0.1 M Py+0.1 M PSS+0.1 M HNO$_3$, 0.1 M Py+ 0.015 M HNO$_3$, 0.6 M Py+0.1 M HNO$_3$. Incorporation control of PSS and acidified nitric acid contribute to improve surface coverage, conductivity and roughness of Ppy films while excess 0.1 M Py monomer condition results in higher roughness.

Conclusions

Direct electrodeposition of Ppy on Al and its alloys is a challenge due to the wide bandgap (electrically insulating) oxide on its surface. Nitric acid is known to produce defects (pits) in the oxide and these appear to facilitate nucleation and growth of Ppy films in the presence of polyanions such as PSS. Increasing the concentration of PSS reduced both the nucleation potential and growth potential and decreased the transition time between nucleation and growth. EDS indicated that

PSS was incorporated as the dopant in the PSS films and also that higher concentrations of PSS (> 50 mM) led to complete coverage of the alloy surface. As expected, the conductivity of the Ppy/PSS films measured by C-AFM increased as the PSS concentration in the electrodeposition solution (hence, doping level in the polymer) was increased. Uniformly conducting films were obtained for films formed from solutions containing 0.1 M each Ppy and PSS. Film thickness and adhesion were relatively independent of PSS concentration greater than 10 mM.

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