Langmuir **1997,** *13,* 1388−1391

Inhibition of Electrochemical Reactions at Gold Surfaces by Grafted, Highly Fluorinated, Hyperbranched Polymer Films

Mingqi Zhao, Yuefen Zhou, Merlin L. Bruening, David E. Bergbreiter,[*,†] and
Richard M. Crooks[*,‡]

Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

Received October 21, 1996. In Final Form: January 21, 1997[⊗]

We report the synthesis and passivation properties of surface-grafted, highly fluorinated, hyperbranched poly(acrylic acid) (PAA) films that contain up to 50 atom % F. These films are very hydrophobic (water contact angle of up to 114°) and block electrochemical reactions on gold electrodes. Cyclic voltammetry in basic solution shows that while an electrode covered with a three-layer PAA (3-PAA) film mimics an assembly of microelectrodes, a fluorinated three-layer PAA (3-PAA/F) film blocks nearly all electron transfer to the gold surface. The charge transfer resistance of electrodes covered with a 3-PAA/F film is about 40 times greater than that for an electrode covered with a nonfluorinated 3-PAA film. 3-PAA/F films are initially 10 times more blocking than $C_{16}SH$ SAMs. Additionally, while the SAM is desorbed by electrochemical cycling, 3-PAA/F films are still highly blocking after ten potential sweeps over a 1.5 V range. Thus fluorinated PAA films are promising candidates for corrosion-inhibiting coatings.

Introduction

Here we report that hydrophobic, highly fluorinated, hyperbranched poly(acrylic acid) (PAA) films effectively passivate metal surfaces. For example, ac-impedance measurements obtained in basic solution show that fluorinated PAA films confined to Au surfaces are about 10^4 times more effective at blocking electrochemical reactions than are the mercaptoundecanoic acid (MUA) monolayers onto which they are grafted.

To prepare PAA films, we first graft poly(*tert*-butyl acrylate) onto a Au-confined MUA monolayer. Hydrolysis of the *tert*-butyl esters then yields a PAA graft and additional grafting at multiple $-CO_2H$ sites on each prior graft leads to hyperbranched PAA films.[1] We previously demonstrated that derivatization of the $-CO_2H$ groups of PAA films with $H_2NCH_2(CF_2)_6CF_3$ yields a fluorinated film.[2,3] Now we show that a subsequent activation of unreacted $-CO_2H$ groups in a fluorinated film followed by reaction with $H_2NCH_2(CF_2)_6CF_3$ produces an even more highly fluorinated film that is quite stable and highly passivating.

Because corrosion is an important problem worldwide, there are many strategies for corrosion passivation including deposition of thin, passivating metal, metal oxide, and organic coatings.[4,5] The development of self-assembled monolayers (SAMs) showed that even ultrathin layers of highly organized material can block electrochemical reactions and in certain cases reduce the rate of corrosion.[6−10] SAMs are attractive because they are strongly linked to the substrate and are amenable to coating objects having unusual geometries as well as on-line modification where spin and dip coating are impractical. However the durability and corrosion resistance of SAMs are limited.[6−15] Alkylsiloxane polymers grafted onto alcohol-terminated SAMs provide better corrosion resistance than SAMs, but the thickness and corrosion resistance of these two-dimensional coatings are also limited.[16−18] We are developing fluorinated, hyperbranched PAA films that are much more durable and blocking than SAMs (*vide infra*). Their ability to span substrate defects should make them excellent corrosion passivation layers even on geometrically complex objects.

Experimental Section

Film Preparation. Three-layer PAA (3-PAA) films and fluorinated 3-PAA (3-PAA/F) films were prepared as described previously.[3] Mercaptoundecanoic acid (MUA) and hexadecyl mercaptan ($C_{16}SH$) SAMs on Au-coated Si(111) wafers were prepared by immersing plasma-cleaned substrates in either ethanolic 0.001 M MUA for 30 min or ethanolic 0.001 M $C_{16}SH$ for 72 h and then rinsing the films with EtOH and water. 3-PAA/2F films were prepared by activating a cleaned 3-PAA/F film with chloroformate and again allowing it to react with $H_2NCH_2(CF_2)_6CF_3$. Prior to electrochemical measurements, any loosely bound material was removed from the films by immersion in 0.1 M HCl in EtOH for 5 min, sonication in $CHCl_3$ for 5 min, and rinsing in EtOH.

---

[*] Authors to whom correspondence should be addressed.

[†] Phone: 409-845-3437. Fax: 409-845-4719. E-mail: bergbreiter@chemvx.tamu.edu.

[‡] Phone: 409-845-5629. Fax: 409-845-1399. E-mail: crooks@chemvx.tamu.edu.

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1997.

(1) Zhou, Y.; Bruening, M. L.; Bergbreiter, D. E.; Crooks, R. M.; Wells, M. *J. Am. Chem. Soc.* **1996**, *118*, 3773.

(2) Zhou, Y.; Bruening, M. L.; Bergbreiter, D. E.; Crooks, R. M. *Langmuir* **1996**, *12*, 5519.

(3) Bruening, M. L.; Zhou, Y.; Aguilar, G.; Agee, R.; Bergbreiter, D. E.; Crooks, R. M. *Langmuir* **1997**, *13*, 770.

(4) *Fundamental Aspects of Corrosion Protection By Surface Modification*; McCafferty, E., Clayton, C. R., Eds.; The Electrochemical Society: Pennington, NJ, 1984; Vol. 84-3, p 355.

(5) Fontana, M. G.; Greene, N. D. *Corrosion Engineering,* 2nd ed.; McGraw-Hill: New York, 1978, p 465.

(6) Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 9022.

(7) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.

(8) Yamamoto, Y.; Nishihara, H.; Aramake, K. *J. Electrochem. Soc.* **1993**, *140*, 436.

(9) Li, Y.-Q.; Chailapakul, O.; Crooks, R. M. *J. Vac. Sci. Technol., B* **1995**, *13*, 1300.

(10) Zamborini, F. P.; Crooks, R. M. *Langmuir* **1997**, *13*, 122.

(11) Finklea, H. O.; Snider, D. A.; Fedyk, J.; Sabatani, E.; Gafni, Y.; Rubinstein, I. *Langmuir* **1993**, *9*, 3660.

(12) Widrig, C. A.; Chung, C.; Porter, M. D. *J. Electroanal. Chem.* **1991**, *310*, 335.

(13) Walczak, M. M.; Popenoe, D. D.; Deinhammer, R. S.; Lamp, B. D.; Chung, C.; Porter, M. D. *Langmuir* **1991**, *7*, 2687.

(14) Weisshaar, D. E.; Walczak, M. M.; Porter, M. D. *Langmuir* **1993**, *9*, 323.

(15) Tarlov, M. J.; Newman, J. G. *Langmuir* **1992**, *8*, 1398.

(16) Itoh, M.; Nishihara, H.; Aramaki, K. *J. Electrochem. Soc.* **1994**, *141*, 2018.

(17) Itoh, M.; Nishihara, H.; Aramaki, K. *J. Electrochem. Soc.* **1995**, *142*, 3696.

(18) Itoh, M.; Nishihara, H.; Aramaki, K. *J. Electrochem. Soc.* **1995**, *142*, 1839.

S0743-7463(96)01016-5 CCC: $14.00

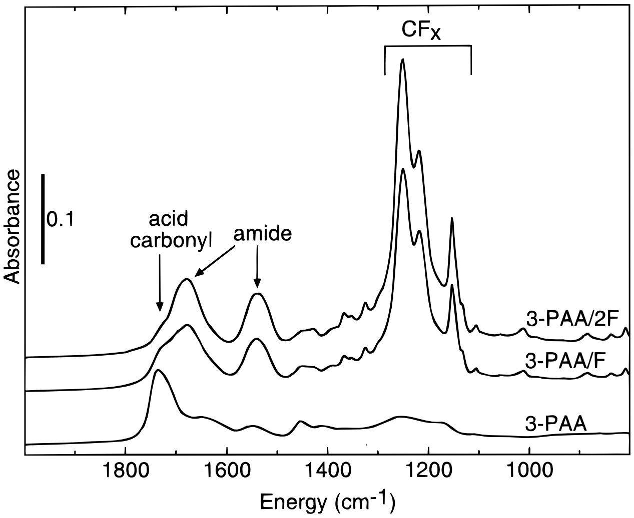

Figure 1. FTIR-ERS spectra of a three-layer PAA film before fluorination (3-PAA) and after one (3-PAA/F) and two (3-PAA/2F) cycles of activation with ethyl chloroformate and reaction with $H_2NCH_2(CF_2)_6CF_3$.

Analysis. Cyclic voltammetric and ac-impedance measurements were performed in a five-necked, three-electrode cell using a Ag/AgCl (3 M NaCl) reference electrode (Bioanalytical Systems, West Lafayette, IN) and a Pt gauze counter electrode, which was separated from the main compartment by a porous glass plug. The working electrode was cut from a Au-coated Si(111) wafer (e-beam evaporated Au (200 nm) on an adhesion layer of 5 nm Ti) and contained within a Teflon/O-ring holder that exposed an area of 0.09 cm^2. Impedance measurements were performed using an EG&G PARC 273A potentiostat and a Solartron 1255 frequency response analyzer controlled by a microcomputer running ZPLOT software (Scribner Associates, Charlottesville, VA). Measurements were performed at 5 mV (root mean squared) around $E°$ (270 mV) of the $Fe(CN)_6^{4-/3-}$ couple, and impedance values were determined at five discrete frequencies per decade. The range of frequencies applied was 0.01 Hz to 65 kHz. Results were analyzed using ZPLOT and ZSIM/CNLS software packages. Cyclic voltammetric measurements were carried out using a BAS Model 100B electrochemical analyzer (Bioanalytical System, Inc.).

All experiments were performed in pH 9.9 buffer (0.2 M NH_4OH + 0.036 M NH_4Cl) containing 1.0 M KCl as supporting electrolyte. This pH was chosen to facilitate comparison between the data presented here and future corrosion experiments employing cyanide, which must necessarily be completed in basic electrolyte solutions. Solutions were purged with N_2 prior to measurements, and during ac-impedance experiments the solution was purged with N_2 at the rate of about two bubbles per second. During cyclic voltammetry experiments, N_2 was blown over the solution. X-ray photoelectron spectroscopy (XPS), Fourier transform infrared-external reflection spectroscopy (FTIR-ERS), ellipsometric thickness, and contact-angle measurements were described previously.[3]

Results and Discussion

Synthesis of Highly Fluorinated Films. We previously reported the fluorination of 3-PAA films with $H_2NCH_2(CF_2)_6CF_3$ through a single cycle of $-CO_2H$ activation and subsequent reaction with $H_2NCH_2(CF_2)_6CF_3$.[2] XPS elemental analysis showed that the surface of these films contains 46 atom % F. Reactivation of the 3-PAA/F film followed by reaction with $H_2NCH_2(CF_2)_6CF_3$ yields a 3-PAA/2F film that contains 50 atom % F, which represents 93% of the theoretical maximum expected in a homopolymer of $(CH_2CHCONHCH_2(CF_2)_6CF_3)_n$. FTIR-ERS spectra (Figure 1) also show an increase in fluorination upon a second cycle of activation and reaction with $H_2NCH_2(CF_2)_6CF_3$. The absorbance of peaks due to CF_x stretching modes increases by approximately 40% after a second reaction with $H_2NCH_2(CF_2)_6CF_3$. Moreover, amide peaks (1680 and 1550 cm^{-1}) arising from the coupling reaction increase after the second fluorination reaction, and the peak due to the acid carbonyl of unreacted $-CO_2H$ groups (1730 cm^{-1}) is reduced in intensity. The surface energy of 3-PAA/F films also decreases after a second fluorination. Water contact angles on PAA films increase from 25° to 109° after one fluorination reaction and to 114° after a second fluorination. Taken together, the XPS, FTIR-ERS, and contact angle results confirm a highly fluorinated, low-surface-energy film.

Table 1. Average Charge-Transfer Resistances (R_{ct}), Apparent Surface Coverages (θ), and Fractional Active Area ($1 - \theta$) of Naked Au and Au Coated with MUA, 3-PAA, 3-PAA/F, and 3-PAA/2F Films in 5 mM $Fe(CN)_6^{3-/4-}$ (pH = 9.9, 1.0 M KCl)

electrode	film thickness (Å)	R_{ct} ($\Omega \cdot cm^2$)	θ	$1 - \theta$
Au	0	1.11 ± 0.03[a]	0	1
Au/MUA	13	4.2 ± 0.9[a]	0.74	0.26
Au/3-PAA	300	$(1.9 \pm 0.6) \times 10^3$ [b]	0.99942	5.8×10^{-4}
Au/3-PAA/F	600	$(80 \pm 50) \times 10^3$ [b]	0.999986	1.4×10^{-5}
Au/3-PAA/2F	700	$(26 \pm 11) \times 10^3$ [b]	0.999957	4.3×10^{-5}

[a] R_{ct} was obtained by fitting the data to Randles' equivalent circuit using ZSIM software. The solution resistance was 60 Ω. [b] R_{ct} was obtained using ZPLOT software to fit the semicircle at intermediate frequencies.

Impedance Analysis of PAA-Coated Electrodes. Organic films confined to electrodes can affect charge-transfer resistance (R_{ct}), interfacial capacitance, mass transport of reactants to the electrode surface, and the apparent heterogeneous rate constant for electron transfer ($k°$). Impedance analysis is a powerful tool that sometimes leads to a straightforward determination of diffusion and kinetic constants for electrochemical systems. This technique is especially well-suited for studies of thin films because the very small ac perturbation (in this case 5 mV rms) causes only minimal changes in the coverage or structure of the film.[19-21]

Figure 2 shows complex-impedance plots at many frequencies for naked and MUA-, $C_{16}SH$-, 3-PAA-, 3-PAA/F-, and 3-PAA/2F-coated Au electrodes in a pH 9.9 buffer solution containing 5 mM $Fe(CN)_6^{3-}$ and 5 mM $Fe(CN)_6^{4-}$. The plot for naked Au reveals a barely discernible semicircle at high frequencies and a 45° line characteristic of Warburg diffusion.[22] The dominance of the Warburg impedance indicates that the redox reaction is diffusion-controlled. For the MUA-covered electrode, we observe a larger-diameter semicircle accompanying the mass transfer-limited behavior at lower frequencies. We used Randles' equivalent circuit to model these systems, and thus the diameter of the semicircle is equal to R_{ct}.[21,23-25] The much larger diameter of the semicircle for 3-PAA-, 3-PAA/F-, and 3-PAA/2F-covered electrodes demonstrates the enhanced barrier properties of these films. As shown in Table 1, the average R_{ct} for the 3-PAA/F film is 40 times greater than that of the already passivating 3-PAA film

---

(19) Hunter, T. B.; Tyler, P. S.; Smyrl, W. H.; White, H. S. *J. Electrochem. Soc.* **1987**, *134*, 2198.

(20) Rubinstein, I.; Sabatani, E. *J. Electrochem. Soc.* **1987**, *134*, 3078.

(21) Sabatani, E.; Rubinstein, I. *J. Phys. Chem.* **1987**, *91*, 6663.

(22) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; John Wiley & Sons, Inc.: New York, 1980; p 718.

(23) Sabatani, E.; Cohen-Boulakia, J.; Bruening, M.; Rubinstein, I. *Langmuir* **1993**, *9*, 2974.

(24) Sabatani, E.; Rubinstein, I.; Maoz, R.; Sagiv, J. *J. Electroanal. Chem.* **1987**, *219*, 365.

(25) In the application of Randles' equivalent circuit to polymer-coated electrodes, the capacitance is a composite of both the film capacitance and the double-layer capacitance. We assumed that the resistance parallel to this capacitance is equal to R_{ct}, but there may be a small contribution from the pore resistance.

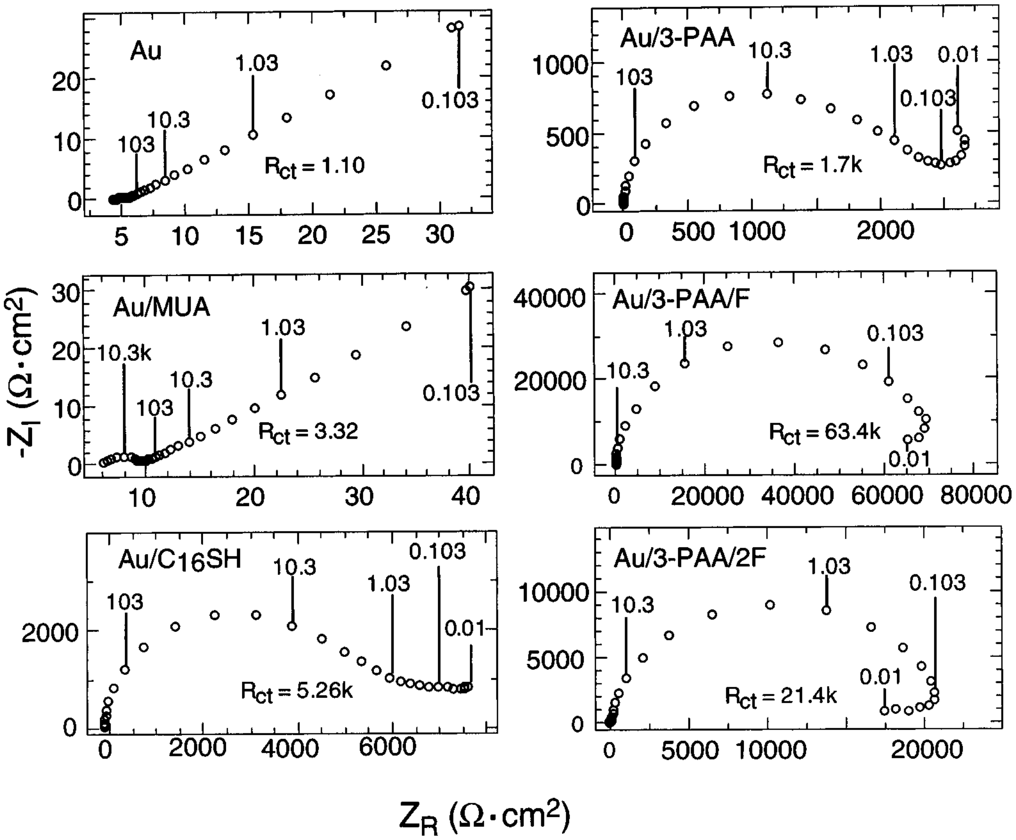

Figure 2. Plots of complex impedance at many frequencies (Hz) for nominally naked Au and 3-PAA-, 3-PAA/F-, and 3-PAA/2F-coated Au electrodes in a pH 9.9 buffered aqueous solution containing 5 mM $Fe(CN)_6^{3-}$ and 5 mM $Fe(CN)_6^{4-}$.

Table 2. Charge-Transfer Resistance[a] and Surface Coverage of $C_{16}SH$, 3-PAA/F, and 3-PAA/2F Films before and after Cyclic Potential Sweeps

no. of potential sweeps[b]	$C_{16}SH$		3-PAA/F		3-PAA/2F	
	R_{ct} (Ω·cm^2)	$1 - \theta$	R_{ct} (Ω·cm^2)	$1 - \theta$	R_{ct} (Ω·cm^2)	$1 - \theta$
0	5.3×10^3	2.0×10^{-4}	47×10^3	2.0×10^{-5}	21×10^3	5.0×10^{-5}
2	37	2.9×10^{-2}	12×10^3	9.0×10^{-5}	9.1×10^3	1.2×10^{-4}
4	4.3	0.25	11×10^3	1.0×10^{-4}	9.5×10^3	1.2×10^{-4}
10	1.1	1.0	11×10^3	1.0×10^{-4}	9.2×10^3	1.2×10^{-4}

[a] R_{ct} was determined using ac-impedance measurements as described in the Experimental Section and the data come from one representative film. [b] The potential is swept from 1000 to −500 mV (vs Ag/AgCl, scan rate of 50 mV/s) in 5 mM $Fe(CN)_6^{3-}$ (pH = 9.9, 1.0 M KCl). Before and after the potential sweeps, the electrode was rinsed in 18 MΩ·cm water.

and 10^4 times greater than the MUA monolayer. The 3-PAA/F film is also 10 times more blocking than a $C_{16}SH$ monolayer (Table 2), which itself has an excellent capacity for blocking electrode reactions.[7] Interestingly, 3-PAA/2F films are comparable or slightly worse at blocking electrode reactions than 3-PAA/F films even though the surfaces of 3-PAA/2F films are more hydrophobic. We think that this results from a change in film morphology during the second cycle of activation and reaction with $H_2NCH_2(CF_2)_6CF_3$. This change may be due to phase segregation of the hydrophobic side chains.

We estimated the effective fractional surface coverage of the polymer (θ) using eq 1 where $R_{ct}°$ is the charge transfer resistance of bare gold.[21] This equation derives from a pinhole model

$$\theta = (R_{ct} - R_{ct}°)/R_{ct} \qquad (1)$$

based on a heterogeneous Au surface. A fraction of the electrode ($1 - \theta$) is composed of naked Au which is accessible to the redox couple. Electron transfer at these sites is characterized by the $k°$ for $Fe(CN)_6^{3-/4-}$. The remaining fraction of the electrode (θ) is assumed to be completely covered by the film and is therefore unavailable for electron transfer. Table 1 lists θ values for the different modified electrodes. Although all of the films grow from a relatively permeable MUA SAM, coverage greatly increases with the addition of 3-PAA, 3-PAA/F, and 3-PAA/2F polymer layers.

Figure 3 shows cyclic voltammetry of several film-covered electrodes in a pH 9.9 buffered aqueous solution containing 5 mM $Fe(CN)_6^{3-}$ obtained using scan rates ranging from 10 to 500 mV/s. Voltammetry of the 3-PAA/F-coated electrode consists mainly of charging current showing that this film effectively blocks electron transfer at the electrode interface. The plateau currents of the $C_{16}SH$- and 3-PAA-coated electrodes change very little as a function of scan rate. This behavior is characteristic of radial diffusion to an assembly of noninteracting microelectrodes.[24,26-28] The steady-state currents of $C_{16}SH$-coated electrodes are larger than those of 3-PAA/F- and 3-PAA/2F-coated electrodes as expected from the active areas of these electrodes determined by ac-impedance analysis.

---

(26) Finklea, H. O.; Snider, D. A.; Fedyk, J. *Langmuir* **1990**, *6*, 371.

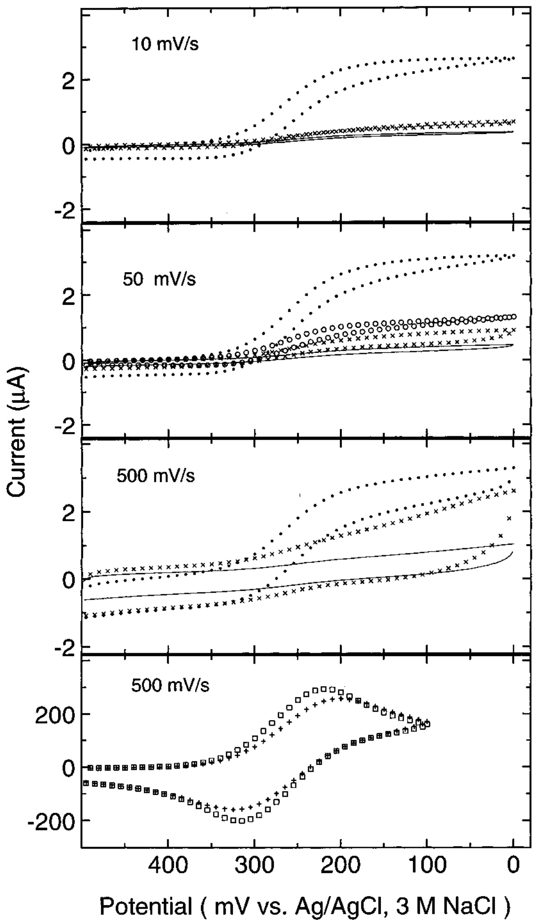

Figure 3. Cyclic voltammetry of nominally naked Au (□) and MUA-coated (+), 3-PAA-coated (●), 3-PAA/F-coated (—), and 3-PAA/2F-coated (×) Au electrodes in a pH 9.9 buffered aqueous solution containing 5 mM $Fe(CN)_6{}^{3-}$. The 50 mV/s frame also shows cyclic voltammetry of a $C_{16}SH$-coated Au electrode for comparison (○).

3-PAA/F films are also more durable than $C_{16}SH$ monolayers. Table 2 shows the large decrease in R_{ct} of a $C_{16}SH$-coated Au electrode that occurs after scanning the electrode potential to extreme values. In these experiments we first measured R_{ct} using ac-impedance analysis, then we obtained cyclic voltammograms between 1000 and −500 mV at a rate of 50 mV/s and repeated the R_{ct} measurement. Two potential sweeps reduced R_{ct} of the $C_{16}SH$-coated Au electrode by a factor of 140 while the R_{ct} of the 3-PAA/F- and 3-PAA/2F-coated electrodes decreased by factors of only 4 and 2, respectively. Increasing the number of potential sweeps (up to 10) eliminates all blocking at the $C_{16}SH$-coated Au substrate but has no measurable effect on the R_{ct} of 3-PAA/F- and 3-PAA/2F-coated electrodes. These results are consistent with other studies showing the reductive and oxidative desorption of thiols.[11−15] The excellent durability of the 3-PAA/F films makes them very attractive for corrosion-passivation applications.

Conclusions

The extent of surface passivation by 3-PAA films and their derivatives increases in the order 3-PAA < 3-PAA/2F < 3-PAA/F. Cyclic voltammetry and ac-impedance measurements show that the fluorinated films provide effective barriers to redox reactions. Any remaining electron transfer occurring at the electrode surface takes place at an assembly of microelectrodes as shown by cyclic voltammetry. Although 3-PAA/2F films contain larger quantities of perfluoroalkanes and have higher contact angles than PAA/F films, blocking decreases slightly upon the second fluorination. This is likely due to a change in film morphology. Unlike organomercaptan SAMs, fluorinated PAA films are stable to potential cycling over a 1.5 V range. The durability and blocking characteristics of fluorinated PAA films make them attractive for corrosion passivation. Additionally, the layer-by-layer grafting of PAA films on SAMs provides good adhesion to the substrate as well as control over film thickness and composition even on complex topographies.

Acknowledgment. We are grateful for financial support of this research from the Office of Naval Research (R.M.C.), the National Science Foundation (D.E.B.: DMR-9634196) and the State of Texas (Higher Education Coordinating Board) through the Advanced Technologies Program. M.L.B. acknowledges a NIH postdoctoral fellowship.

LA961016Z

---

(27) Amatore, C.; Savéant, J. M.; Tessier, D. *J. Electroanal. Chem.* **1983**, *147*, 39.

(28) Gileadi, E. *Electrode Kinetics for Chemists, Chemical Engineers, and Materials Scientists*; VCH Publishers, Inc.: New York, 1993, pp 451.