Inhibition of Al Alloy Corrosion by Chromates

by Gerald S. Frankel and Richard L. McCreery

So what's the big deal about Al corrosion? A recent literature search indicated that about 45 papers have been published in *J. Electrochem. Soc.* alone over the past five years in the area of Al and Al alloy corrosion (not including work related to batteries and microelectronics). Numerous symposia on localized corrosion and light alloy corrosion have taken place over this time period with large numbers of presentations on the mechanisms of localized corrosion in structural Al alloys and its inhibition by chromates and environmentally friendly inhibitors. Interest in these topics has existed for a long time, but the recent flurry of activity was initiated by the U.S. Air Force (USAF) around 1996. For decades, the USAF had considered corrosion of aircraft to be a topic of minor importance that could be handled by small modifications to fracture mechanics solutions for structural integrity. Eventually, it became clear that corrosion of airframes was the most costly maintenance problem for Air Force aging aircraft.[1] The annual cost of corrosion to the USAF is commonly quoted as being about $1,000,000,000.

There are a few key aspects to the USAF corrosion problem:

- The USAF fleet is aging and aircraft are now required to serve long beyond their intended lifetimes (in years) because replacement with new aircraft is too costly. Aircraft lifetime is typically limited by fatigue associated with total flying time and flight cycles. Many of these aircraft are young in terms of their fatigue life because military planes are used relatively infrequently. However, between missions, they sit on runways exposed to the environment and corrode. The periodic maintenance performed on airplanes to repair corrosion damage is lengthy and expensive.
- The structural components of aircraft are largely fabricated from high strength Al alloys that contain alloying elements such as Cu, Mg, Fe, and Mn. These alloying additions provide strength, but also segregate to form intermetallic compound (IMC) particles. The heterogeneous microstructure of high strength Al alloys makes them particularly susceptible to localized corrosion, such as pitting, crevice, intergranular, and exfoliation corrosion.
- These high strength Al alloys can only be used in corrosive environments with the help of protective coating systems that have traditionally contained Cr^{VI} species. Chromates and dichromates are extremely effective inhibitors of Al alloy localized corrosion. However, as many people are now aware in this age of Erin Brokovich, chromates are carcinogenic, expensive to handle, and create a difficult disposal problem. The use of chromates might soon be tightly restricted by environmental regulation. Environment-friendly replacements for chromates have been developed, but none are as effective as chromate for inhibition of high strength Al alloys.[2]

In 1995, a blue ribbon advisory panel recommended that the USAF devote significant resources to investigate a number of topics, including the definition of mechanisms of Al corrosion and chromate inhibition/replacement.[3] The intent was to assist development of a more effective and environment-friendly chromate replacement by generating a better understanding of how chromate works. The USAF Office of Scientific Research responded by funding numerous projects on Al alloy corrosion, inhibition, and protection over the past five years, including two Multi-University Research Initiative (MURI) programs, one of which has been based at The Ohio State University. Other U.S. agencies, such as the Defense Advanced Research Projects Agency (DARPA), Department of Energy (DOE), and Strategic Environmental Research and Development Program (SERDP), have also funded programs in these areas, so that the total effort has been quite large.

In what follows, we will summarize our views on chromate inhibition of Al alloys. We will not attempt to incorporate all of the views of even our own MURI team colleagues, let alone the entirety of the body of knowledge that has developed over the past few years. Our intent here is to identify the major scientific issues, and to report on recent progress toward understanding corrosion protection by chromate coatings.

The important components of Al alloy inhibition by chromate are storage and release of Cr^{VI} species, inhibition of cathodic reactions (primarily oxygen reduction), and inhibition of attack at active sites in the alloy. These areas will be addressed in turn. First, a brief discussion of the corrosion mechanisms of Al alloys is appropriate.

A variety of forms of corrosion can occur on coated structures fabricated from high strength Al alloys, as shown in Fig. 1. Chromate can be present in a chromate conversion coating (CCC) or as a pigment in the primer. The uncoated area to the left is meant to represent the phenomena

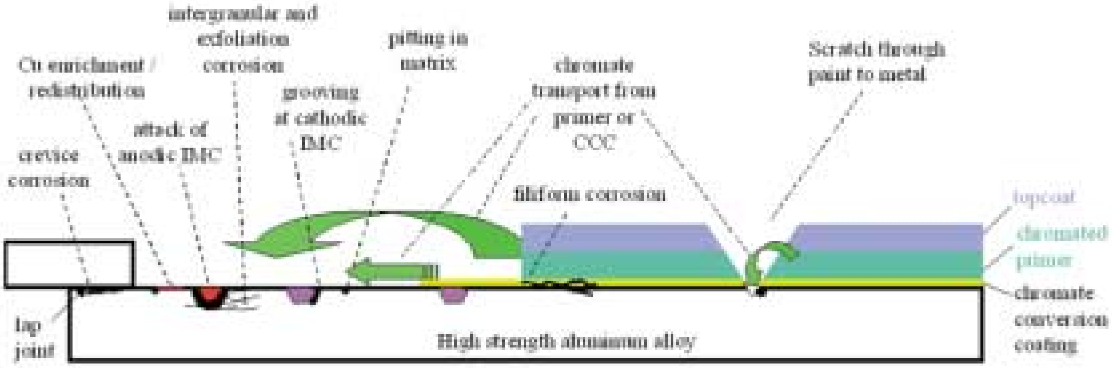

Fig. 1. Schematic of corrosion of coated high strength Al alloy structure and transport of chromate from primer or CCC.

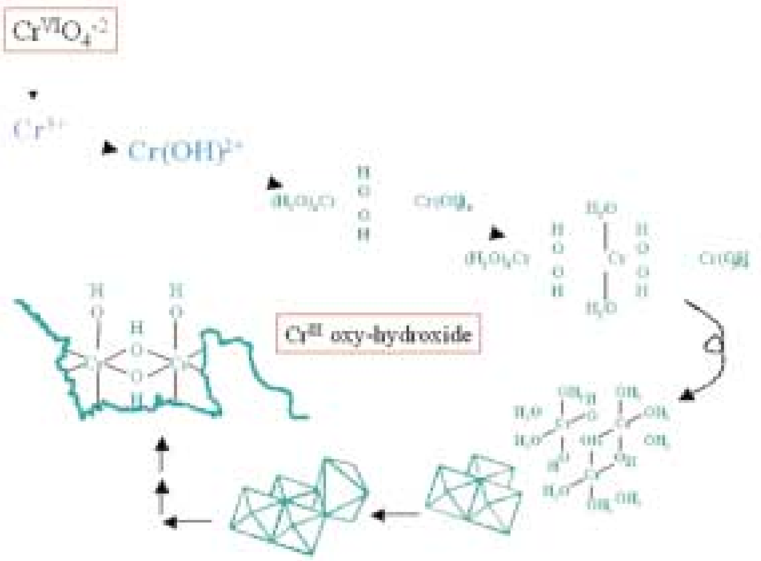

FIG. 2. Polymerization of Cr^{III} following reduction of Cr^{VI} during CCC formation. The product is a hydrated Cr^{III} oxide, often referred to as Cr^{III} oxy-hydroxide. The polymerization reaction is faster for high Cr^{III} concentration and higher pH.[11,12,14,15]

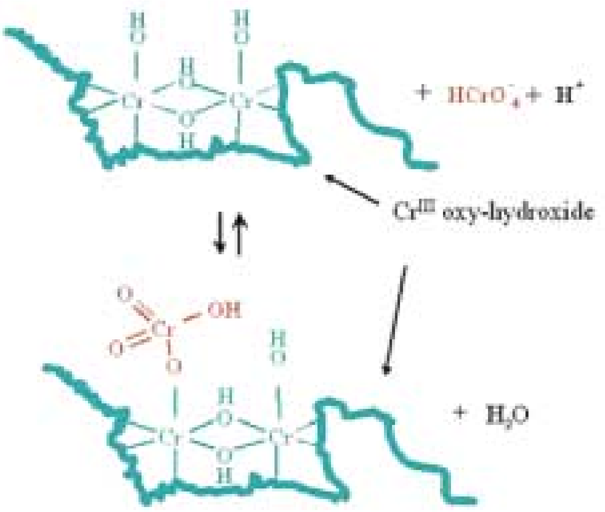

FIG. 3. Equilibrium between solution phase Cr^{VI} ($MCrO_4^-$) and Cr^{VI} bound to Cr^{III} oxy-hydroxide. Jagged line represents the surface of Cr^{III} oxy-hydroxide. Cr^{VI} may bind as a monomer or dimer, but the structure shown is the most likely.

that can occur on an exposed metal surface, such as might happen at the base of a scratch through the coating system, as shown on the right. The IMCs can be cathodic (primarily supporting cathodic reactions), anodic (corroding themselves), or fluctuate between the two conditions as they react and change. Cu can enrich on the surface away from the IMCs owing to redistribution from the IMCs[4] or by dealloying of the Al matrix.[5] Enriched Cu sites can be effective cathodes, driving corrosion at anodic sites, including anodic IMCs, matrix sites, and crevices, which exist in aircraft at lap joints. The localized corrosion attack can be in the form of pitting, crevice, intergranular, exfoliation, or filiform corrosion. Many of these forms of corrosion can initiate stress corrosion cracks.

A valuable and remarkable property of chromate coatings is "self healing" or "active corrosion inhibition," in which metal exposed at the base of scratch or defect through the protective coating is protected, possibly years after the coating was applied.[6-9] Both the CCC and $SrCrO_4$-containing primers are able to store chromate, then release it if damage occurs to provide self healing. This phenomenon is shown schematically in Fig. 1 as green arrows. Spectroscopic monitoring of CCCs revealed that they release Cr^{VI} upon exposure to water or salt solution, and that this Cr^{VI} may migrate to regions of untreated or scratched alloy.[9,10] Cr^{VI} is stored in the CCC as a Cr^{III}/Cr^{VI} mixed oxide, which is essentially a matrix of Cr^{III} oxy-hydroxide with covalent Cr^{III}-O-Cr^{VI} linkages to chromate anions. The nature of the Cr^{VI}/Cr^{III} mixed oxide is shown in Figs. 2 and 3.[8,11] During CCC formation, Cr^{VI} is reduced to Cr^{III}, which undergoes a series of condensation reactions to produce a hydrated Cr^{III} oxy-hydroxide, Fig. 2.[11-13] The relatively high Cr^{III} concentration present during CCC formation promotes the Cr^{III} polymerization reaction,[14,15] which occurs within the several minute time scale of typical CCC formation. As the Cr^{III} oxy-hydroxy polymer is forming in what amounts to a sol-gel process, it binds Cr^{VI} as shown in Fig. 3. The binding of Cr^{VI} to Cr^{III} to form a mixed oxide is reversible, with the equilibrium Cr^{VI} concentration governed by an expression similar to a Langmuir isotherm.[10] In the presence of high Cr^{VI} concentration during CCC formation, Cr^{VI} binding is favored, resulting in a mixed oxide that is approximately 25% Cr^{VI} and 75% Cr^{III}.[8,11]

Upon exposure to water or salt solution, a CCC releases Cr^{VI} to a level of approximately 10^{-4} M, depending on solution volume and CCC area. The release of Cr^{VI} from a CCC is favored both by the low solution concentration of Cr^{VI} expected in field applications, and by the relatively high pH which might be present near cathodic sites.[10] This released Cr^{VI} then diffuses to a defect and interacts with bare metal or metal oxide. In the case of $SrCrO_4$ containing primers, Cr^{VI} is provided by the solubility of $SrCrO_4$, yielding a solution Cr^{VI} concentration of approximately 10^{-3} M at equilibrium. The storage and release of Cr^{VI} by a CCC or $SrCrO_4$ pigment are important properties of chromate anticorrosion coatings, because they are the basis of the unusual self-healing property.

The chromate transported to the exposed metal sites acts to inhibit corrosion. Corrosion inhibitors are chemicals added to solution or a surface treatment that results in the reduction in the rate of the corrosion process. Inhibition is classified as being anodic, cathodic, or mixed, depending on which part of the full corrosion reaction is primarily reduced. Anodic inhibition of localized corrosion might result from the reduction of either the initiation or propagation stage of the localized attack. Spatially resolved Raman spectroscopy has shown recently that CCC film thickness varies over intermetallic phases in AA2024-T3,[13] and that dilute Cr^{VI} in solution deposits selectively near corrosion pits.[16]

Recent work has shown that chromate does not effectively reduce the rate of localized corrosion propagation in Al or Al alloys. For example, the penetration rate of localized corrosion through AA2024-T3 foils in 1 M NaCl was unaffected by the addition of 0.1 M $Na_2Cr_2O_7$ under an applied anodic potential.[17] However, at the open circuit potential in 1 M NaCl containing only 1 mM $Na_2Cr_2O_7$, the localized attack was eliminated, which is evi-

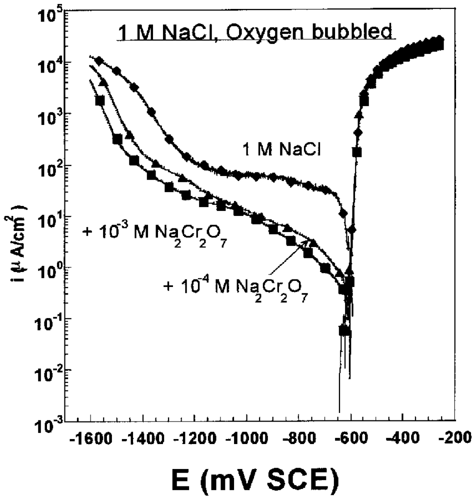

FIG. 4. Polarization curves for AA2024-T3 in oxygen bubble 1 M NaCl containing various amounts of $Na_2Cr_4O_7$.[17]

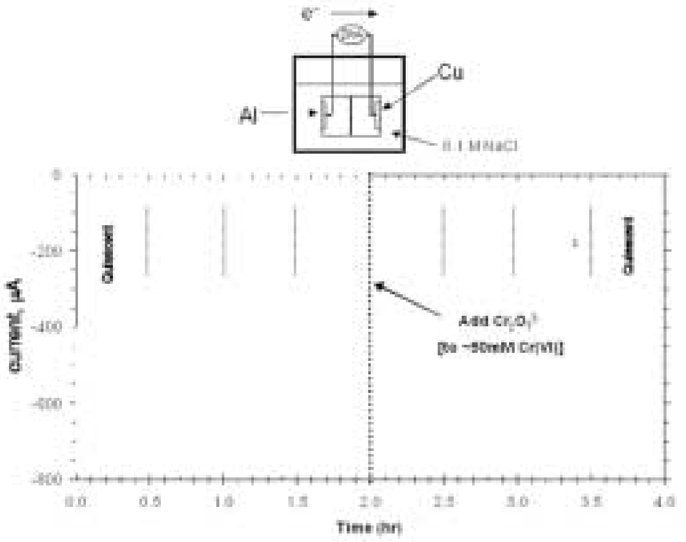

FIG. 5. Current for an Al/Cu galvanic couple in 0.1 M NaCl. ZRA is a zero resistance ammeter, and negative current indicates electron flow toward the Cu electrode.[21]

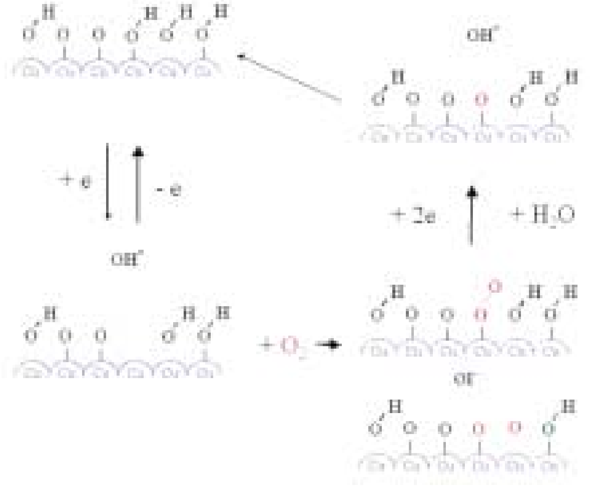

FIG. 6. An example of a catalytic cycle for O_2 reduction which involves chemisorption of O_2 or its reduction products to bare copper atoms on the alloy surface. This mechanism is one of many possibilities and is intended only to illustrate a possible role of chemisorption.

dence for cathodic inhibition as described below. The influence of chromate on active dissolution of Al was also studied using the artificial crevice technique.[18,19] Of chromate, dichromate, molybdate, and nitrate, only nitrate was found to inhibit the dissolution kinetics of Al artificial crevice electrodes. In contrast, all anions inhibited the dissolution kinetics of Mg artificial crevice electrodes. The results indicate that the mechanism of localized corrosion inhibition of Al alloys by chromate must be something other than inhibition of anodic dissolution in an active pit or crevice. In fact, under certain conditions, chromate can act like an oxidizing agent and enhance the rate of localized corrosion. AFM scratching of pure Al in a stagnant solution of 0.5 M NaCl + 10^{-4} M $Na_2Cr_2O_7$ resulted in the formation of large pits, in contrast to the accelerated uniform dissolution during AFM scratching of Al in 0.5 M NaCl with no dichromate.[20]

Considerable evidence has been developed during recent years to indicate that chromate inhibits the cathodic reaction (oxygen reduction in particular) on Al alloys and forms a protective film that inhibits localized corrosion initiation. Figure 4 shows polarization curves for AA2024-T3 in 1 M NaCl bubbled with oxygen.[17] The anodic and cathodic portions of the polarization curve were measured separately from the open-circuit potential. A clear decrease in the rate of oxygen reduction is observed with as little as 10^{-4} M added $Na_2Cr_2O_7$.

A more graphic illustration of cathodic inhibition by Cr^{VI} is shown in Fig. 5, which plots the current flowing from an Al anode to a Cu cathode acting as a galvanic couple in salt solution.[21] Removal of O_2 by Ar saturation reduces the galvanic current to near zero, while O_2 saturation causes significant Al oxidation. Addition of Cr^{VI} dramatically decreases the observed current, and the current remains low even after Cr^{VI} is removed from the solution. This observation may be explained by either cathodic or anodic inhibition by Cr^{VI}. However, related experiments in a split cell reveal that the Cr^{VI} is irreversibly reduced to Cr^{III} on the Cu cathode, and that this Cr^{III} layer is a powerful O_2 reduction inhibitor.[21]

O_2 reduction is one of the most-studied electrochemical reactions on a variety of electrodes, due in part to its fundamental importance and because O_2 is the most common oxidizer for fuel cells. The O_2 reduction mechanism is very complex, involving 2-4 e^- and 2-4 H^+ ions, depending on the products and conditions.[22-27] Chemisorption of O_2 or its partially reduced intermediates is usually involved, hence the common use of noble metals as electrocatalysts in fuel cells. An example of a catalytic cycle involving chemisorption of oxygen is shown in Fig. 6, in this case on a copper surface. The O_2 reduction rate is a complex function of catalyst surface area, chemisorption energy and kinetics, and accompanying solution reactions. Although the mechanism may change significantly on different metals, there is general agreement that chemisorption is a key step for catalyzing O_2 reduction. If Cr^{VI} adsorbs to catalytic sites, it will inhibit O_2 reduction and provide corrosion protection. Furthermore, Cr^{VI} adsorption is likely followed by irreversible reduction to Cr^{III}, which "locks in" the inhibitor, to permanently interfere with O_2 reduction.

The sites responsible for O_2 reduction in AA2024 and the mechanism of inhibition by Cr^{VI} are not yet clear, but some important clues are available. The alumina passive film on pure Al prevents O_2 reduction, hence the well-known corrosion resistance of pure Al. However, Cu-rich inclusions in AA2024 are capable of O_2 reduction, and they comprise a small percentage of the surface area.[4] Although the sites and detailed mechanism of Cr^{VI} inhibition of O_2 reduction are subjects of current investigations, it is clear that the mobility, adsorption, and irreversible reduction of Cr^{VI} on potential cathodic sites are key components of both the corrosion protection and self healing provided by chromate containing coatings.

Insight into the role of chromate as both an anodic and cathodic inhibitor for Al alloy corrosion is provided by experiments on small areas containing different regions of the microstructure of AA2024-T3 exposed to the environment through masking windows.[28] Small rectangular areas, on the order of tens of microns on a side, were exposed to solution by creating a mask with a thin polymeric film and scratching through the film with an AFM tip to create an opening. Different parts of the microstructure were also exposed simultaneously using two windows. A 60 min exposure to 0.5 M NaCl of a window positioned within an AlCuFeMn particle or containing only matrix phase with no large intermetallic particles resulted in no corrosion to the limit observable by AFM. In contrast, exposure of a window containing both AlCuFeMn and matrix resulted in significant attack, the extent of which increased as the percentage of AlCuFeMn in the exposed area increased. This indicates that both anodic and cathodic sites are required for localized corrosion to occur. Interestingly, an area containing Al_2CuMg S phase particles and matrix did not corrode, indicating that such particles were not efficient cathodes.

If an area of AlCuFeMn particle was exposed to a dichromate solution prior to exposing a second window of matrix and immersion in chloride solution, the corrosion was prevented. Similarly, pre-exposure of a window containing matrix phase to dichromate resulted in no corrosion when the area was subsequently and simultaneously exposed to chloride solution with a window containing AlCuFeMn phase. These observations indicate that dichromate exposure results in the formation of a film that is both an anodic and cathodic inhibitor in the sense that it decreases the activity of both anodes and cathodes.

AFM scratching is another means to show how chromate reduces the activities of the active IMC particles. This technique involves rastering an AFM tip in contact mode across the surface of a sample immersed in solution to stimulate depassivation.[20,29] AFM scratching of AA2024-T3 in 0.01 M NaCl results in immediate dissolution of the Al_2CuMg S phase particles owing to the removal of the oxide film, which provides some protection.[29] However, in 0.5 M NaCl containing only 10^{-4} M $Na_2Cr_4O_7$, the attack of the S phase particles is completely suppressed during AFM scratching.[20] The film that forms on these anodic particles is particularly protective.

In summary, there are several reasons why chromate is an extremely effective corrosion inhibitor for Al alloys:

1. Chromate can be stored in conversion coatings and as a pigment in paints.
2. Chromate is released from these coatings, particularly when they are scratched to refresh the coating area. The released chromate is in equilibrium with the chromate in the coatings, and higher pH favors CrVI release.
3. Chromate is mobile in solution and migrates to exposed areas on the Al alloy surface.
4. Chromate adsorbs on the active sites of the surface and is reduced to form a monolayer of a Cr^{III} species.
5. This layer is effective at reducing the activity of both cathodic sites (Cu-rich IMC particles) and anodic sites in the matrix or at S phase particles. The anodic inhibition is related to the initiation stage of localized corrosion and not propagation.
6. The combined properties of storage, release, migration, and irreversible reduction provided by chromate coatings underlie their outstanding corrosion protection.
7. Inhibition of the oxygen reduction reaction at cathodic Cu-rich IMC particles is an important part of the overall corrosion inhibition mechanism.

It is reasonable to expect that replication of these characteristics of chromate using another inhibitor species is necessary to successfully replace chromate as a critical component for Al alloy corrosion inhibition. ■

Acknowledgments

This work was supported by the United States Air Force Office of Scientific Research under contract No F49620-96-1-0479.

References

1. Aging of U.S. Aircraft, Final Report, Committee on Aging of U.S. Air Force Aircraft, National Materials Advisory Board, National Academy Press, Washington, DC (1997).
2. Alternatives to Chromium for Metal Finishing, National Center for Manufacturing Sciences, Ann Arbor (1995).
3. USAF Blue Ribbon Advisory Panel Report on Aircraft Coatings, Materials Directorate, Wright Laboratory (1995).
4. R. G. Buchheit, R. P. Grant, P. F. Hlava, B. McKenzie, and G. L. Zender, *J. Electrochem. Soc.*, **144**, 2621 (1997).
5. N. Dimitrov, J. A. Mann, and K. Sieradzki, *J. Eletrochem. Soc.*, **146**, 98 (1999).
6. H. A. Katzman, G. M. Malouf, R. Bauer, and G. W. Stupian, *Appl. Surf. Sci.*, **2**, 416 (1979).
7. M. A. Heine and M. J. Pryor, *J. Electrochem Soc.*, **114**, 1001 (1967).
8. F. W. Lytle, R. B. Greegor, G. L. Bibbins, K. Y. Blohowiak, R. E. Smith, and G. D. Tuss, *Corros. Sci.*, **37,** 349 (1995).
9. J. Zhao, G. S. Frankel, and R. L. McCreery, *J. Electrochem. Soc.*, **145**, 2258 (1998).
10. L. Xia, E. Akiyama, G. S. Frankel, and R. L. McCreery, *J. Electrochem Soc.*, **147**, 2556 (2000).
11. L. Xia, and R. L. McCreery, *J. Electrochem. Soc.*, **145**, 3083 (1998).
12. L. Xia. and R. L. McCreery, *J. Electrochem Soc.*, **146**, 3696 (1999).
13. W. R. McGovern, P. Schmutz, R. G. Buchheit, and R. L. McCreery, *J. Electrochem Soc.*, **147**, 4494 (2000).
14. H. Stunzi and W. Marty, *Inorg. Chem.*, **22**, 2145 (1983).
15. H. Stunzi and W. Marty, *Inorg. Chem.*, **28**, 66 (1989).
16. J. D. Ramsey and R. L. McCreery, *J. Electrochem Soc.*, **146**, 4076 (1999).
17. A. Sehgal, G. S. Frankel, B. Zoofan, and S. Rokhlin, *J. Electrochem. Soc.*, **147**, 140 (2000).
18. Q. Meng, T. Ramgopal, and G. S. Frankel, *Electrochem. Solid-State Lett.*, in press.
19. E. Akiyama and G. S. Frankel, *J. Electrochem. Soc.*, **146**, 4095 (1999).
20. P. Schmutz and G. S. Frankel, *J. Electrochem. Soc.*, **146**, 4461 (1999).

21. W. J. Clark, J. D. Ramsey, R. L. McCreery, and G. S. Frankel, *J. Electrochem Soc.*, Submitted.
22. N. Markovic and P. N. Ross, in *Electrocatalysis at Well-Defined Surfaces: Kinetics of Oxygen Reduction and Hydrogen Oxidation/Evolution on Pt (hkl) Electrodes, in Interfacial Electrochemistry*, A. Wieckowski, Editor, *p. 82*, Dekker, New York (1999).
23. R. Adzic, *Electrocatalysis*, J. Lipkowski and P. N. Ross, Editors, Wiley-VCH, New York (1998).
24. T. Yano, E. Popa, D. A. Tyrk, K. Hashimoto, and A. Fujishima, *J. Electrochem. Soc.*, 146, 1081 (1999).
25. H.-H. Yang and R. L. McCreery, *J. Electrochem. Soc*, 147, 3420 (2000).
26. D. T. Sawyer, *Oxygen Chemistry*, Oxford University Press, London (1991).
27. A. E. Martell and D. T. Sawyer, *Oxygen Complexes and Oxygen Activation by Transition Metals,* Plenum Press, New York (1988).
28. P. Leblanc and G. S. Frankel, *J. Electrochem Soc.,* Submitted.
29. P. Schmutz and G. S. Frankel, *J. Electrochem. Soc.,* 145, 2298 (1998).

About the Authors

__Jerry Frankel__ is the Director of the Fontana Corrosion Center at The Ohio State University in Columbus, OH. He can be reached at frankel.10@osu.edu.

__Richard McCreery__ is Dow Professor of Chemistry at The Ohio State University, with research interests in spectroscopy applied to electrode surfaces, molecular electronics, and anticorrosion films on aluminum alloys.