

Inhibition Effects of Chromate, Phosphate, Sulfate, and Borate on Chloride Pitting Corrosion of Al

Hochun Lee* and Hugh S. Isaacs†

Battery R&D, LG Chem Ltd., Moonji-dong, Yooseong-gu, Daejeon 305-380, South Korea

†Condensed Matter Physics & Materials Science Department, Brookhaven National Laboratory, Upton, NY 11973, U.S.A.

(Received August 13, 2008 : Accepted August 18, 2008)

Abstract : Inhibitive effects of chromate, phosphate, sulfate, and borate on chloride pitting corrosion of Al have been investigated using cyclic voltammetry. During the anodic oxide growth, the critical concentration of chloride for pit initiation decreased in the order: chromate > phosphate > sulfate > borate, and the maximum pitting current density increases in the reverse order: chromate < phosphate < sulfate < borate. The decreasing pitting current density was observed in the successive polarization cycles, which was attributed to the aging of Al oxides and field relaxation at oxide/solution interface.

Keywords : Aluminum, Pitting, Chloride, Inhibition, Cyclic voltammetry.

1. Introduction

Many investigators have reported inhibition effects of inorganic anions such as chromate, phosphate, sulfate, tungstate, molybdate, nitrite, and nitrate for pitting corrosion in Al.¹⁻⁵⁾ In a quite early report, Anderson and Hocking suggested that chromate and phosphate anions compete with chloride for adsorption site on the Al oxide surface.¹⁾ Böhm and Uhlig claimed that the efficiency of pitting inhibition decreases in the order: nitrate > chromate > acetate > benzoate > sulfate, which was interpreted in terms of competitive adsorption between inhibitive and aggressive ions.²⁾ Konno and his co-workers suggested that chromate and phosphate anions adsorb on Al oxide surface hindering penetration of water molecule and preventing deterioration of the oxide.³⁾ Lee and Pyun observed that sulfate ion impedes the initiation of pit below the pitting potential, but enhances the growth of pre-existing pits.⁴⁾ The inhibition effects of chromate, tungstate, molybdate, nitrite, and nitrate have also been compared using chronoamperometric measurement toward chloride pitting corrosion of Al and Al-Si alloy.⁵⁾

Recently, we demonstrated the applicability of simple cyclic voltammetry (CV) to determine the growth

and dissolution characteristics of pure Al oxide in near neutral borate, chromate, phosphate, and sulfate solutions.^{6,7)} In a borate and a chromate solution, the currents continued to decrease with each subsequent cycle due to oxide thickening. In contrast, a significant rate of oxide dissolution occurred to produce reproducible repetitive curves during subsequent cycles in a phosphate and a sulfate solution. Below the pitting potential the CV technique has also been found by White and co-workers to be a very versatile tool to examine the dissolution behavior of Al oxide in borate solutions with added chloride.^{8,9)} They found that the dissolution rate increased with increased chloride concentration and depended on crystal orientation and grain boundaries yielding the sequence polycrystalline Al > Al(111) ~ Al(110) > Al(100).

Potentiodynamic polarization measurement has long been used to characterize the potential at which pitting initiates.^{1,10)} However, no details have been presented as to the effect of chloride on the cyclic voltammetric behavior in the above electrolyte solutions. This study compares the pitting susceptibility of pure Al in chromate, phosphate, sulfate, and borate solutions using cyclic voltammetry. It is hoped that this study will eventually lead to a better understanding of the pit initiation/inhibition mechanism by aggressive/inhibitive anions.

*E-mail: dukelee@lgchem.com

2. Experimental

A high purity Al (99.9999%, Cominco Electronic Materials) in the shape of a square rod with a cross sectional area of 1 cm^2 was used. The surface of the Al rod was first anodized to 100 V at a constant current density of 2 mA/cm^2 in borate solution (pH 8.0) for electrical insulation. Prior to testing, the cross section of the rod was abraded down to a 600 grit SiC paper while wetted with deionized (DI) water. After the abrasion, it was washed well with DI water and dried in air. The abraded end of Al rod was immersed in solution to a depth of about 2 mm during the measurements. The solutions were made with analytical grade reagents and DI water.

0.5 M borate ($\text{H}_3\text{BO}_3/\text{Na}_2\text{B}_4\text{O}_7$), phosphate ($\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$), chromate ($\text{K}_2\text{CrO}_4/\text{K}_2\text{Cr}_2\text{O}_7$), and sulfate (Na_2SO_4) solutions were used. In order to obtain pH 7.0, the relative composition was varied for the former three solutions, while NaOH was added for sulfate solution.

During testing the solutions were held at $20.0 \pm 0.2^\circ\text{C}$ and freely exposed to air. The scan rate was fixed at 5 mV/s . A saturated mercury sulfate reference electrode (0.39 V more positive than a saturated calomel electrode) and a platinum counter electrode were used.

3. Results and Discussion

Fig. 1 shows the cyclic voltammograms (CVs) of abraded pure Al in chromate solution (pH 7.0) with varying Cl^- concentration from 0 to 50 mM. In Cl^- -free chromate (Fig. 1a), the current increases rapidly and then reaches a plateau region during the first anodic scan. When the scanning direction is reversed at -0.3 V and the potential decreases, the current drops rapidly and approaches zero. Note the current at the positive potential limit (-0.3 V) continues to decrease during the subsequent cycles. This is because the oxide thickness increases during each cycle. The polarization behavior in the chromate can be accounted for in terms of the high field conduction model without chemical oxide dissolution.⁶⁾ Small current spikes begin to appear at the first cathodic scan around 33 mM Cl^- (Fig. 1b), below which voltammetric behavior is not affected significantly by the presence of Cl^- . As Cl^- concentration increases above the threshold value (Fig. 1c and Fig. 1d), the pitting initiates during the first anodic scan and keeps growing even after the scanning direction is reversed. After reaching the maximum, the pitting current drops rapidly and approaches to zero around -1.0 V . Note that the pitting current keeps decreasing in the subsequent

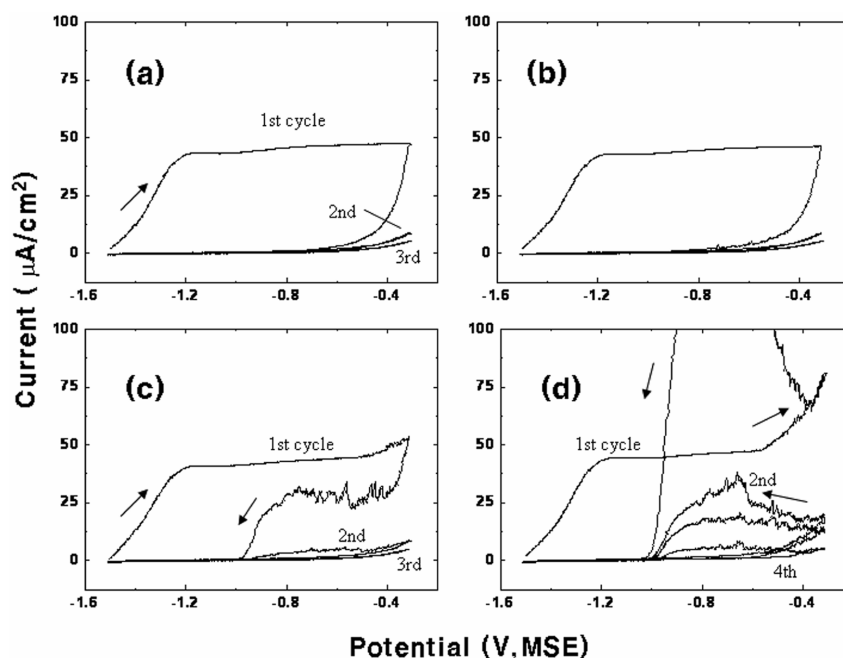


Fig. 1. Cyclic voltammograms of freshly abraded Al in 0.5 M chromate (pH 7.0) containing NaCl of (a) 0 mM, (b) 33 mM, (c) 45 mM, and (d) 50 mM.

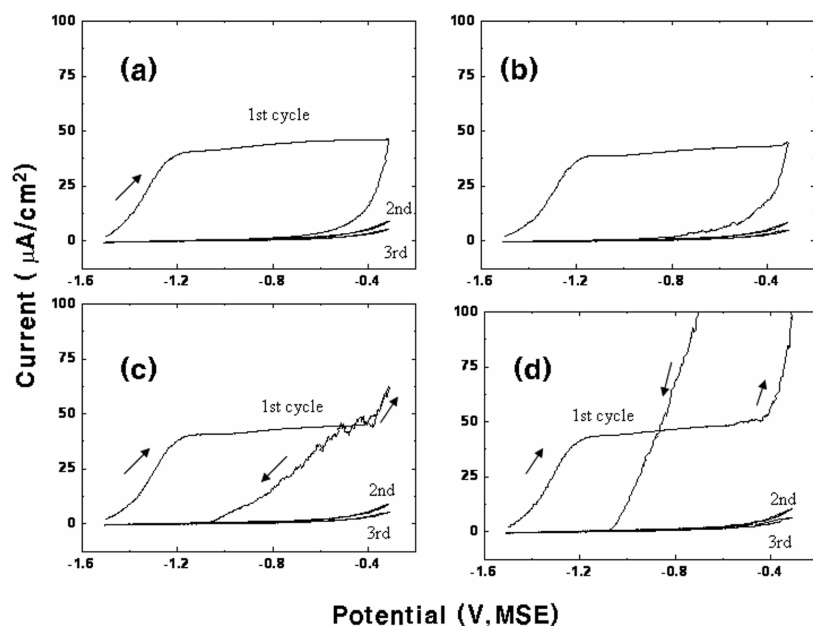


Fig. 2. Cyclic voltammograms of freshly abraded Al in 0.5 M borate (pH 7.0) containing NaCl of (a) 0 mM, (b) 0.5 mM, (c) 0.7 mM, and (d) 0.8 mM.

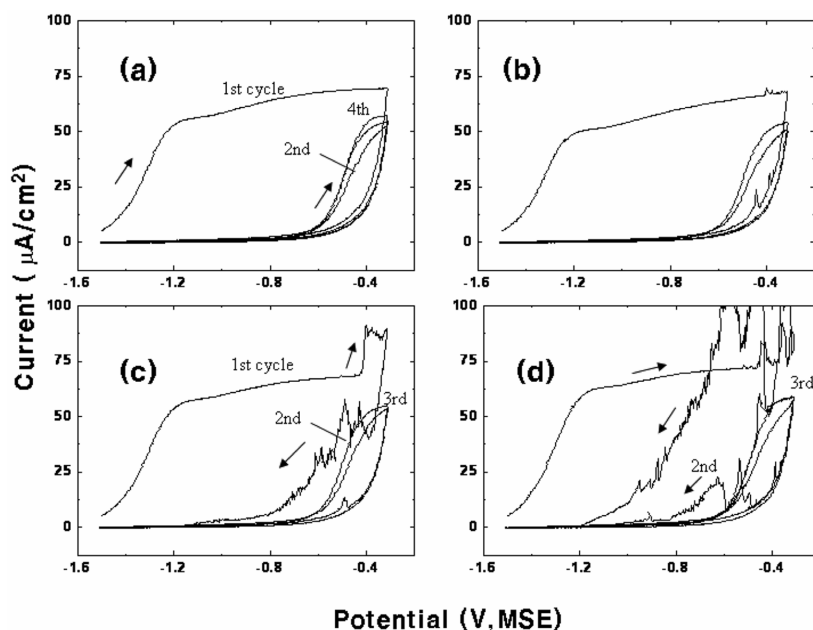


Fig. 3. Cyclic voltammograms of freshly abraded Al in 0.5 M phosphate (pH 7.0) containing NaCl of (a) 0 mM, (b) 25 mM, (c) 30 mM, and (d) 35 mM.

cycles. The possible explanations will be given in the following discussion section.

The CV in a Cl^- -free borate (Fig. 2a) is very similar

to that in a Cl^- -free chromate (Fig. 1a), which indicates similar characteristics of oxide growth and negligible dissolution of oxide in both solutions. However, the

effect of the presence of Cl^- in the borate is much more prominent than that in the chromate. About 0.5 mM Cl^- (Fig. 2b), compared with 33 mM in the chromate, is the threshold concentration to initiate pitting in the borate and intense pitting occurs above 0.7~0.8 mM Cl^- (Fig. 2c and 2d). Thus, the borate has much less pitting inhibition effect than the chromate despite their similarity in the oxide growth and dissolution characteristics.

In a Cl^- -free phosphate (Fig. 3a), the current response in the first cycle is similar to those in the chromate and the borate. However, the current again increases to a considerable value during the subsequent cycles. These characteristics indicate additional anodic oxide formation taking place that compensates the loss of oxide caused by dissolution, which can be understood in terms of the high field conduction model with oxide dissolution.⁶⁾ The pitting starts to occur around the threshold Cl^- concentration of 25 mM (Fig. 3b), which is smaller than 33 mM in the chromate but higher than 0.5 mM in the borate. Again, each subsequent cycle shows decreasing pitting susceptibility.

In a Cl^- -free sulfate (Fig. 4a), the first cycle shows no plateau and the current continues to rise almost linearly with potential during the first anodic scan. The subsequent cycles exhibit intermediate characteristics

between those in the borate and the phosphate. Recently, we have revealed that the behavior in sulfate solution is consistent with an increase in local acidity at oxide/solution interface resulting from the Al anodization.⁷⁾ By assuming that the oxide formation efficiency decreases with surface acidity due to field assisted dissolution, we were able to numerically simulate the sulfate behavior. The dissolution rate in the sulfate was found to be smaller than that of the phosphate, but larger than those of the chromate and the borate. As shown in Fig. 4b, around Cl^- concentration of 12 mM, the pitting starts to occur and larger pitting current is observed above the threshold concentration (Fig. 4c and 4d).

Fig. 5 shows the variation of the maximum pitting current during the first cathodic scan (i_{max}) against Cl^- concentration. Note that i_{max} at the same Cl^- concentration increases in the order: chromate < phosphate < sulfate < borate. This result, together with the fact that order of the critical Cl^- concentration for pit initiation, indicates that pitting inhibition ability decreases in the order: chromate > phosphate > sulfate > borate. To authors' knowledge, this is the first comparison between the pitting inhibition abilities among these anions. Note that the pitting inhibition ability and oxide dissolution rate are correlated in the series of phosphate > sulfate > borate.

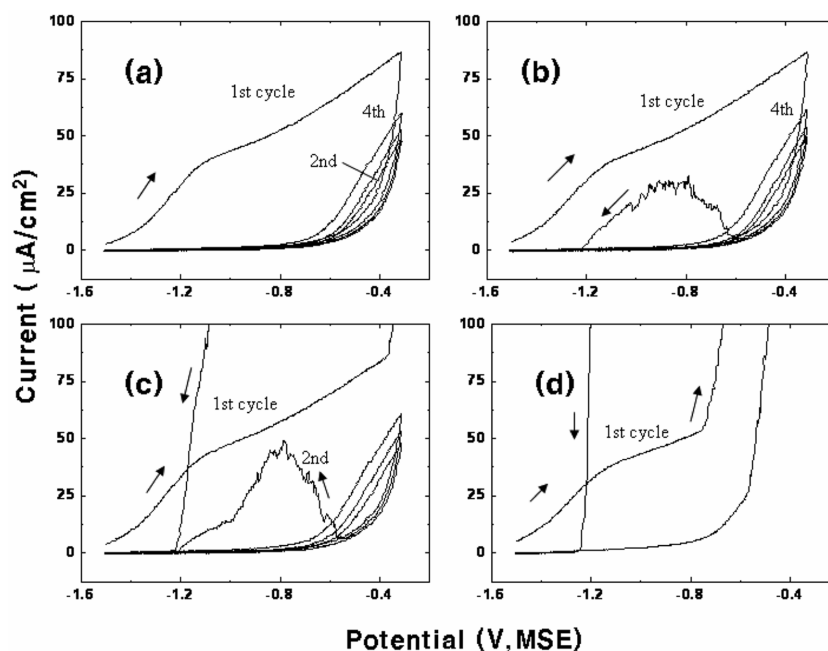


Fig. 4. Cyclic voltammograms of freshly abraded Al in 0.5 M sulfate (pH 7.0) containing NaCl of (a) 0 mM, (b) 12 mM, (c) 14 mM, and (d) 20 mM.

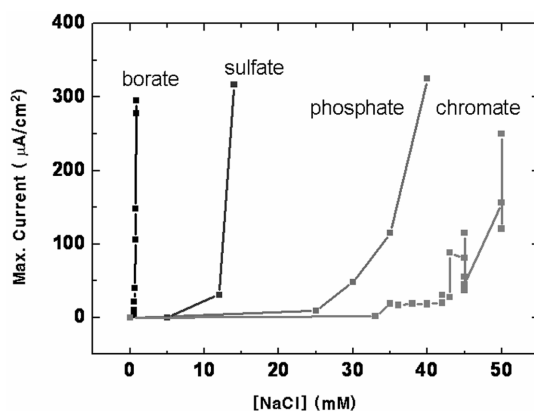


Fig. 5. Maximum pitting current density during the first cathodic scan (i_{\max}) vs. [NaCl] in borate, sulfate, phosphate, and chromate.

It seems that absorbed Cl^- is removed along with the surface oxide at the oxide/solution interface, which makes pitting difficult to occur in oxide-dissolving solutions. The prominent inhibition ability of chromate, however, cannot be accounted for in terms of the ability of oxide dissolution. Regarding the unique inhibition ability of chromate, many groups have devoted extensive efforts but its mechanism still remains unclear.¹¹⁾

In the previous section, it is noted that the pitting susceptibility keeps decreasing in successive cycles. Several different investigators have noticed similar behavior. Kim and Buchheit has reported that pitting potentials of pure Al and Al-2Cu alloy increase by potential cycling within the range of $-0.6 \sim -0.75$ V, which is attributed to the defect healing by passive dissolution.¹²⁾ Lee and Pyun and observed that pre-immersion of pure Al in chloride solution under the open circuit condition reduced the number of available pit initiation sites, which was ascribed to the occurrence of meta-stable pitting.¹³⁾ In addition, the decreasing pitting current in the successive voltammetric cycle has also been reported in non-aqueous solutions, which was explained by the formation of corrosion product in the oxide defect sites making further dissolution difficult.¹⁴⁾ Thus, decreasing pitting susceptibility in pre-treated samples seems to be due to the inactivation or healing of defect sites existing on the incipient oxide. Possible reasons for the inactivation of defect sites during the pretreatment process have been considered: oxide thickening, oxide aging with time, and field relaxation during the cathodic scan.

In order to check these possibilities, the potential scan was stopped at -0.6 V and the potential was set to open

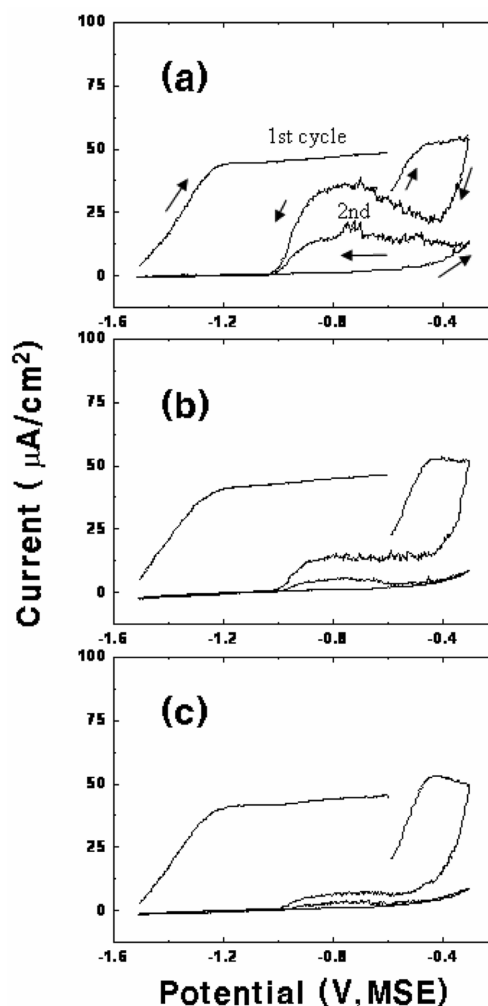


Fig. 6. Cyclic voltammograms of freshly abraded Al in 0.5 M chromate (pH 7.0) containing 60 mM NaCl. The first anodic scan was stopped at -0.6 V and rested at OCP for (a) 1 min., (b) 4 min., and (c) 8 min., then resumed from -0.6 V.

circuit potential (OCP) during the first anodic scan in the chromate containing 60 mM Cl^- . After resting at OCP for 1, 4, and 8 min., the potential scan was resumed from -0.6 V and following current response was measured. As shown in Fig. 6, resting at OCP significantly decreases the pitting susceptibility. For example, i_{\max} is 38 A/cm^2 after resting at OCP for 1 min. (Fig. 6a), which is much smaller than that in a normal potential scan (158 mA/cm^2 in Fig 1d). These results enable us to exclude the possibility of oxide thickening because there was no additional anodic oxide formation during OCP condition. In addition, i_{\max} decreases further to 16 and

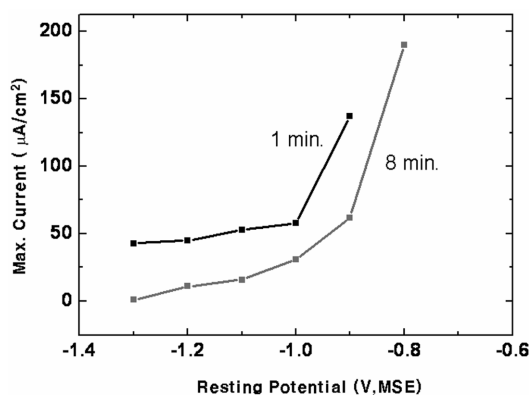


Fig. 7. Maximum pitting current density during the first cathodic scan (i_{\max}) vs. resting potential. The first anodic scan was stopped at -0.6 V and rested at pre-set potential for (a) 1 min. and (b) 8 min., then resumed from -0.6 V.

6 A/cm^2 when the resting time is increased to 4 and 8 min, respectively, which seems to be an evidence of oxide aging with time. However, this may also be due to potential or field relaxation because OCP mainly stays below -1.2 V (not shown here), which is much more negative than -0.6 V. To examine the possibility of the field relaxation, the electrode potential was set to a fixed value between -1.3 and -0.8 V for 1 or 8 min. Note that i_{\max} decreases as the resting potential is decreased (Fig. 7). This clearly shows that the resting potential (or field) plays an important role in determining the pitting susceptibility. The field relaxation seems to be related to expulsion of adsorbed Cl^- or Al-Cl complex from oxide surface by the repulsive electrostatic force. i_{\max} decreases as resting time increases from 1 min. to 8 min. at the same resting potential, which may be due to either oxide aging with time or longer field relaxation time. Thus, both effects of oxide aging with time and field relaxation seem to be at play in decreasing pitting susceptibility of subsequent cycles. Similar result is obtained in the borate containing 0.8 mM Cl^- (not shown here), which excludes the possibility that the decreasing pitting susceptibility with resting potential is due to any specific interaction between the oxide surface and chromate ions.

4. Conclusions

Cyclic voltammetry measurements were made on freshly abraded Al in neutral chromate, phosphate, sulfate, and borate solutions and their inhibition abilities

for pitting by chloride were compared. The inhibition ability decreases in the following order: chromate > phosphate > sulfate > borate, which is the same order as their oxide dissolution rate except chromate. The decreasing pitting current density was observed in the successive polarization cycles, which was attributed to the aging of Al oxides and field relaxation at oxide/solution interface.

References

1. P. J. Anderson and M. E. Hocking, 'On the anodic polarization behavior of aluminum' *J. Appl. Chem.*, **8**, 352 (1958).
2. H. Böhni and H. H. Uhlig, 'Environmental factors affecting the critical pitting potential of aluminum' *J. Electrochem. Soc.*, **116**, 906 (1969).
3. H. Konno, S. Kobayashi, H. Takahashi, and M. Nagayama, 'The hydration of barrier oxide films on aluminum and its inhibition by chromate and phosphate ions' *Corros. Sci.*, **22**, 913 (1982).
4. W. -J. Lee and S. -I. Pyun, 'Effects of sulphate ion additives on the pitting corrosion of pure aluminum in 0.01 M NaCl solution' *Electrochim. Acta*, **45**, 1901 (2000).
5. S. S. Abdel Rehim, H. H. Hassan, and M. A. Amin, 'Chronoamperometric studies of pitting corrosion of Al and (Al-Si) alloys by halide ions in neutral sulphate solutions' *Corros. Sci.*, **46**, 1921 (2004).
6. H. Lee, F. Xu, C. S. Jeffcoate, and H. S. Isaacs, 'Cyclic polarization behavior of aluminum oxide films in near neutral solutions' *Electrochem Solid-State Lett.*, **4**, B31 (2001).
7. H. Lee and H. S. Isaacs, *Electrochim. Acta*, submitted.
8. C. J. Boxley, J. J. Watkins, and H. S. White, 'Al₂O₃ film dissolution in aqueous chloride solutions' *Electrochem Solid-State Lett.*, **6**, B38 (2003).
9. S. Lee and H. S. White, 'Dissolution of the native oxide film on polycrystalline and single-crystal aluminum in NaCl solutions' *J. Electrochem. Soc.*, **151**, B479 (2004).
10. H. Kaesche, in: R.P. Frankenthal, J. Kruger (Eds.), "Passivity of Metals", 935, The Electrochemical Society, New Jersey (1978).
11. H. S. Isaacs, K. Sasaki, C. S. Jeffcoate, V. Laget, and R.G. Buchheit, 'Formation of chromate conversion coatings on aluminum and its alloys' *J. Electrochem. Soc.*, **152**, B441 (2005).
12. Y. Kim and R. G. Buchheit, private communication.
13. W. -J. Lee and S. -I. Pyun, 'Effects of hydroxide ion addition on anodic dissolution of pure aluminum in chloride ion-containing solution' *Electrochim. Acta*, **44**, 4041 (1999).
14. A. G. Muñoz, J. B. Bessone, 'Pitting of aluminum in non-aqueous chloride media' *Corros. Sci.*, **41**, 1447 (1999).