



Electrochemical Evaluation of Constituent Intermetallics in Aluminum Alloy 2024-T3 Exposed to Aqueous Vanadate Inhibitors

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Experiments were conducted to determine how inhibiting forms of vanadate interact with complex Al alloy microconstituent intermetallics to impart corrosion protection. Cathodic polarization experiments on Al 2024-T3 indicate a strong correlation between inhibition and the presence of tetrahedrally coordinated vanadate. Anodic and cathodic polarization curves were measured on bulk synthesized Al₂Cu, Al₂CuMg, Al₇Cu₂Fe, and Al₂₀Cu₂Mn₃ in alkaline 0.5 M NaCl solutions with and without 10 mM NaVO₃. Vanadate additions generally decreased E_{corr} , increased E_{pit} , and decreased the cathodic kinetics of all tested materials. Because of decreased cathodic kinetics, open-circuit potentials (OCPs) were shifted in the active direction in aerated solutions when vanadate was present. This shift pins the OCP just below the observed pitting potential for Al₂CuMg in vanadate solution, effectively preventing breakdown and subsequent support of rapid oxygen reduction by Cu-enriched clusters. E_{corr} , E_{pit} , E_{rp} , i_{corr} , i_{pass} , and i at $-1.3 V_{\text{SCE}}$ data from polarization experiments were summarized in cumulative distribution plots, and averages are presented in tabulated format. Scanning electron microscopy images of Al 2024-T3 used for 4 h of OCP measurement show that vanadate greatly decreased circumferential trenching around intermetallic particles in both aerated and deaerated solutions. Potentiostatic hold experiments were used to show suppression of Al₂CuMg dissolution in vanadate solutions.

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Aluminum 2024-T3 is a high-strength age-hardened aluminum alloy commonly used in the aerospace industry. Al 2024-T3 contains, by weight percent, 3.8–4.9 Cu, 1.2–1.8 Mg, 0.3–0.9 Mn, and small quantities of Si, Fe, Zn, Cr, and Ti.¹ Alloy additions result in both superior mechanical properties and a heterogeneous microstructure which renders the alloy susceptible to localized corrosion.¹ Appreciable quantities of copper, magnesium, and manganese, added as strengtheners, remain in solid solution. However, through heat-treatments and natural aging, a dispersion of fine Cu and Mg particles and insoluble intermetallic precipitates form within the matrix phase. The main constituent particles in Al 2024-T3 include Al₂CuMg, Al₇Cu₂Fe, Al₂Cu, and Al₂₀Cu₂Mn₃. The effect of intermetallic particles on corrosion of aluminum alloys has been widely studied.^{2–11} For Al 2024-T3, it has been found that intermetallics containing Cu are typically noble or become noble to the surrounding aluminum matrix during exposure to many electrolytes, and these particles are capable of supporting rapid cathodic kinetics.^{4,5,8,9,12} Such cathodic particles drive corrosion in the surrounding matrix, leading to pitting and trenching attack morphologies.^{10,11,13} Al₂CuMg (S phase) intermetallic particles are of particular interest, because Al₂CuMg is one of the most abundant intermetallic particles found in Al 2024-T3 and in large part has been found to be responsible for susceptibility of Al 2024-T3 to localized corrosion.^{4,5} The corrosion of Al₂CuMg is complex; under free-corrosion conditions, the intermetallic is initially anodically polarized by the matrix, leading to selective dissolution of Mg from the intermetallic and nonfaradaic liberation of Cu, which can then be oxidized to form ions that can be reduced on the surrounding matrix.^{4,5} Often what remains of the particle is an enriched Cu remnant, which acts as a local cathode, supporting rapid oxygen reduction and corrosion in the surrounding matrix.^{4,5} Prevention of Mg dissolution from Al₂CuMg and, as a result, the subsequent formation of local Cu cathodes capable of supporting rapid oxygen reduction could be an effective way to increase the resistance of Al 2024-T3 to localized corrosion.¹⁴

Historically, chromate-based pigments and coatings have been used successfully to prevent corrosion of aluminum alloys.¹⁵ However, due to environmental and carcinogenic risks associated with chromate use, more “green” alternative inhibitors and coatings have

recently received attention. In particular, soluble vanadates, vanadate-based coatings, and inhibitor pigments have been observed to inhibit the corrosion of aluminum alloys and have shown promise as chromate replacements.^{16–23} However, unlike chromates, aqueous vanadates have a relatively complex aqueous chemistry, dependent on pH, concentration, and ionic strength.^{24–26} This convolutes a straight forward understanding of inhibition. In a simplified description of aqueous vanadate speciation, tetrahedrally coordinated species, metavanadates, and pyrovanadates, predominate in alkaline solutions, octahedrally coordinated species, decavanadates, predominate in acid solutions, and single tetrahedral species exist over a wide pH range at low concentrations. Previous work has shown that the extent of inhibition depends strongly on vanadate speciation, with the greatest inhibition from tetrahedrally coordinated species, which are predominant in alkaline solutions.^{18,20–22,27} Tetrahedrally coordinated vanadates have been shown to act primarily through decreased oxygen reduction; however, vanadates have also been observed to be modest anodic inhibitors independent of aeration.^{18,22} Decavanadate ions, which are combinations of 10 octahedrally coordinated vanadate units, are predominant in acidic solutions of appropriate vanadium concentration and have been shown to be poor inhibitors of oxygen reduction.^{18,20–22,24,25,27} There is evidence that decavanadate increases the cathodic kinetics in acidic NaCl solutions.¹⁸ However, small increases in pH, as found near sites supporting oxygen reduction, can trigger the decomposition of noninhibiting octahedrally coordinated species into inhibiting tetrahedral species, which helps explain corrosion protection observed from pigments containing decavanadate.^{16,18,28,29}

Evidence exists that inhibiting tetrahedrally coordinated vanadates suppress the dissolution of Al₂CuMg intermetallics.^{18,21,27} Ralston et al. noted suppressed Mg dissolution from Cu–Mg particles exposed to alkaline and mildly acidic 50 mM NaCl solutions with NaVO₃ compared to particles exposed to NaVO₃-free solutions.¹⁸ Iannuzzi and Frankel used in situ atomic force microscopy scratching to observe that additions as small as 0.1 mM of metavanadate to 0.5 M NaCl suppressed the attack of Al₂CuMg particles, while corrosion in the surrounding matrix was still observed.²⁷ Iannuzzi further found that 5 mM of metavanadate prevented transient Al₂CuMg dissolution, resulting in increased corrosion resistance at open-circuit potential (OCP).^{20,21} The mechanism of suppression of transient dissolution was not clear, but it was speculated that monovanadates on the matrix prevent or displace Cl[–] adsorption on the surface, which hinders subsequent oxide film breakdown.²⁰ Generally, it is not

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corrosion of Al 2024-T3 through acting exclusively on Al₂CuMg or if suppressed Al₂CuMg dissolution is a consequence of overall corrosion inhibition. Although previous work has established that solutions containing predominately tetrahedrally coordinated vanadates prevent or slow Mg dissolution from Al₂CuMg, and in turn the formation of Cu-rich cathodes capable of supporting rapid oxygen reduction, the precise relationship between tetrahedral vanadates, Al₂CuMg, and the matrix is not currently understood.

Vanadate is a known buffer, and observed inhibition must be rationalized in the context of the effects that buffers have on corrosion. The presence of a buffer can have pronounced effects on the corrosion of Al–Cu alloys.^{30,31} In unbuffered systems, oxygen reduction results in an increase in alkalinity at cathodic sites, which dissolves the surrounding Al matrix, leading to shallow grooving and trenching around intermetallics and, occasionally, widespread cathodic corrosion across the matrix.^{30,31} When a buffer is present, local alkalization and associated cathodic corrosion damage modes are suppressed. However, when these modes are suppressed, the cathodic reaction is then available to support penetrating localized corrosion sites such as acid pits and crevices.^{30,31} This leads to deep and discrete pits but comparatively less mass loss than is observed in unbuffered systems.³⁰

Due to the small size of constituent intermetallic particles present in Al 2024-T3, direct electrochemical testing of different intermetallics in the matrix is not feasible. However, previous work on aluminum alloys using a microcapillary electrode and synthesized “bulk” intermetallics demonstrates that intermetallic-specific electrochemical data can be obtained.^{2,3,32} The microcell is a modified standard three-electrode setup that uses a thin, glass, silicon-coated capillary connected to an electrolyte reservoir, containing both a reference electrode and counter electrode to contact and allow electrochemical experiments on micrometer-scale-diameter working electrodes.^{33,34} General details of the microcell setup and a specific description of the microcell used for this work can be found in the literature.^{33,34} By choosing bulk intermetallics that are representative of constituents in Al 2024-T3, pure Al and Cu, and an Al 4% Cu solid solution used as a matrix analog, electrochemical characteristics of specific intermetallic phases can be catalogued and used to rationalize observed behavior of the bulk alloy.

The objective of this work is to determine how inhibiting vanadates interact with the matrix and constituent particles of Al 2024-T3. In addition, this work aims to develop a deeper understanding of the suppression of Mg dissolution from Al₂CuMg intermetallics in inhibiting vanadate solutions.

Experimental

Solution preparation.— Solutions for all experiments were prepared using reagent-grade chemicals. The NaVO₃ for solution preparation was purchased from Fluka Chemika with an assay of ≥98%. Cathodic polarization experiments were conducted in 0.5 M NaCl solutions adjusted to pH 5.1 using HCl with 0.25 and 0.0025 M NaVO₃ to show the effect that tetrahedral vanadates have on inhibition compared to octahedral vanadates. However, most experiments were conducted in alkaline 0.5 M NaCl solutions with and without 10 mM NaVO₃ to characterize the inhibitive effect tetrahedrally coordinated vanadates have on different constituent intermetallics in Al 2024-T3. The initial as-dissolved 0.5 M NaCl + 10 mM NaVO₃ solution was yellow and had a pH of 6.37. As previously mentioned, vanadates have been shown to provide the strongest inhibition when coordinated tetrahedrally, which occurs in alkaline solutions. As a result, the pH of the master test solution was adjusted with dropwise additions of 10 N NaOH until the pH reached 9.18. Before experimentation, the test solution was allowed to equilibrate for more than 2 weeks, during which a few additional drops of NaOH were used to maintain the pH above 9. Once the pH was stable, nuclear magnetic resonance (NMR) was used to characterize the solution. To help ensure that the vanadate species in solution were not evolving with time, the solution pH was monitored

daily over the course of microcell experimentation, and NMR spectra were collected prior to the first experiment and after completion of the last experiment. The same 0.5 M NaCl + 10 mM NaVO₃ solution was used for subsequent experiments after completion of the microcell polarization work. Because the solution appeared stable over the duration of microcell experiments, pH was used as a sufficient measure of solution and species stability. Although the NaVO₃ solution remained stable, the pH of NaCl solutions adjusted to approximately pH 9.2 decreased with time. This is likely the result of H₂CO₃ formation from dissolved atmospheric CO₂ and the subsequent proton formation from equilibria involving HCO₃⁻ and CO₃²⁻, which both have increased solubility in alkaline solutions.³⁵ As a result, care was taken to monitor and measure the pH immediately prior to and during each testing session. Unless specifically stated, the pH of NaCl-only solutions was between 9.05 and 9.20. Additionally, the reservoir, capillary, and tubing of the microcell were frequently flushed with fresh solution throughout experimentation.

NMR.— Vanadates have a complex aqueous speciation depending on both concentration and pH, and as a result, small changes in pH can have dramatic effects on the type and concentration of specific species in solution. NMR was used to characterize solutions used for cathodic polarization experiments on an Al 2024-T3 sheet in pH 5.1 NaVO₃ solutions and microcell polarization experiments in alkaline 10 mM NaVO₃ solution, which were expected to take a number of weeks to complete and for which the possibility of solution evolution with time was a concern. After allowing approximately 2 weeks for solution stabilization, NMR spectra were collected immediately prior to microcell work in vanadate solutions and 10 days later after completion of experimentation. NMR spectra for cathodic polarization experiments in pH 5.1 solutions were collected immediately after the pH of the vanadate solutions was adjusted. A Bruker DPX 400 MHz superconducting magnet was used to collect high-resolution ⁵¹V (105.2 MHz) NMR spectra. An indirect detection probe was used with a 90° pulse duration of 10.38 μs. Spectra were collected using 8192 transients, a spectral window of 73,529 Hz, a 0.051 s acquisition time, and a 0.20 s relaxation delay. Each spectrum had the subsequent process parameters applied: 10.0 Hz line broadening, zero filling (25 K points), and baseline correction. A solution consisting of 20% v/v VOCl₃ in C₆D₆ (δ⁵¹V = 0 ppm) was used as an external standard to reference the ⁵¹V chemical shifts. Peaks were identified by comparison to literature.^{26,29,36}

Potentiodynamic polarization using the microcapillary electrode.— To characterize the inhibitive effects of tetrahedrally coordinated vanadates, anodic and cathodic polarization curves were collected on representative bulk versions of intermetallics found in Al 2024-T3 in alkaline 10 mM NaVO₃ + 0.5 M NaCl and NaVO₃-free 0.5 M NaCl solutions. Samples used for potentiodynamic polarization experiments using the microcell were sourced from previous work and commercial suppliers. The 99.999% Al and 99.9% Cu samples were obtained from Alfa Aesar. The intermetallic samples used in this study were prepared and studied previously: Al₂Cu₂Fe and Al₂₀Cu₂Mn,³² Al 4%Cu,³ Al₂CuMg,⁴ and Al₂Cu.³⁷ Samples were ground in 200 proof ethyl alcohol to 1 μm using SiC grinding papers, followed by polishing using 6 and 1 μm diamond pastes. All electrochemical experiments presented in this paper were made using an Autolab PGSTAT 100 potentiostat in conjunction with General Purpose Electrochemical Systems data-acquisition software. Both anodic and cathodic polarization experiments were preceded by 30 s of OCP measurement and were carried out in aerated solutions using a 0.01 V/s scan rate. Anodic polarization curves were initiated at -0.03 V vs OCP and reversed at either 0.0 V vs OCP or manually at approximately 0.05 V above any observed breakdown. Cathodic polarization experiments were initiated at 0.03 V vs OCP and terminated at -2.0 V vs saturated calomel electrode (SCE), although capillary tip leaking often resulted in

early termination of the experiment. The contact area used for area normalization of data was estimated from digital images taken after individual experiments.

Electrochemical experiments on bulk Al 2024-T3 sheet.— Experiments on bulk Al 2024-T3 electrodes in alkaline 0.5 M NaCl solutions with and without 10 mM NaVO₃ were used to obtain electrochemical data from the actual alloy for comparison to microcell results. Experiments in pH 5.1 NaVO₃ solutions were used to show the inhibiting effect that tetrahedrally coordinated vanadates have on cathodic kinetics compared to octahedrally coordinated vanadates. Further, work on bulk Al 2024-T3 was used to gain insight into Al₂CuMg dissolution. An Al 2024-T3 sheet was used for four different sets of experiments, cathodic polarization, OCP measurement, anodic polarization, and potentiostatic experiments. All samples were polished by hand in 200 proof ethyl alcohol to at least 1 μm in a similar fashion as discussed for microcell sample preparation except for the samples for OCP measurements, which were polished to 1/4 μm using diamond paste, the samples for potentiostatic experiments, which were polished to 1 μm using a diamond suspension, and the samples used for cathodic polarization, which were polished to 1200 grit under ethyl alcohol. Experiments on a bulk Al 2024-T3 sheet were carried out using a standard three-electrode setup, which included a SCE reference, a platinum counter electrode mesh, and 1 cm² exposed working electrode. Cathodic polarization experiments in actively aerated pH 5.1 NaVO₃ solutions were preceded by a 30 min measurement of OCP. The scan was initiated at 0.03 V vs OCP, and a scan rate of 0.5 mV/s was used. OCP was measured for 4 h in actively aerated and deaerated 0.5 M NaCl solutions at approximately pH 9.2 with and without 10 mM NaVO₃ to determine the effect of tetrahedrally coordinated vanadates on OCP with time. For deaerated OCP measurements, solutions were deaerated for 1 h before the electrolyte came in contact with the sample. Anodic polarization curves on the Al 2024-T3 sheet in 0.5 M NaCl solution with 10 mM NaVO₃ solution at approximately pH 9.17 were used to make comparisons between microcell data and data collected from the Al 2024-T3 sheet. Anodic polarization experiments were preceded by a 30 min measurement of OCP. The scan was initiated at -0.03 V vs OCP, and a scan rate of 0.5 mV/s was used with scan reversal at -0.25 V_{SCE}. Potentiostatic hold experiments were conducted in 0.5 M NaCl solutions between pH 9.1 and 9.23 with and without 10 mM NaVO₃. These experiments were used to determine if tetrahedral vanadates have an effect on the repassivation of the surface once activated and to show the suppression of Mg dissolution from Al₂CuMg intermetallics. Each 100 mL test solution was deaerated for 30 min prior to experimentation and sample exposure. The samples were held at a conditioning potential of 1 V_{SCE} for 1 s and then held at a specific potential for the next 120 s; potential holds at -1.2, -0.9, -0.8, -0.7, -0.6, and -0.5 V_{SCE} were used.

Results

Inhibition from tetrahedral vanadate species vs octahedral species.— The effect that tetrahedrally coordinated vanadates have on cathodic kinetics compared to octahedrally coordinated species can be observed through experiments in mildly acidic NaVO₃ solutions. Figure 1 shows the NMR spectra from two different pH 5.1 0.5 M NaCl solutions with (a) 0.0025 and (b) 0.25 M NaVO₃. The subscript of the peak labels in the figure describes the number of vanadium atoms in each oligomer. For example, V₁ indicates single tetrahedrally coordinated vanadium [VO₄³⁻, VO₃(OH)²⁻, VO₂(OH)₂⁻, VO(OH)₃], V₂ indicates dimeric vanadate [V₂O₇⁴⁻, V₂O₆(OH)³⁻], V₄ is tetrameric (V₄O₁₂⁴⁻, V₄O₁₃⁶⁻), V₅ is pentameric (V₅O₁₆⁷⁻, V₅O₁₅⁵⁻), and V₁₀ represents decameric vanadate species [V₁₀O₂₈⁶⁻, V₁₀O₂₆(OH)₂⁴⁻, V₁₀O₂₇(OH)₅⁻].^{25,26,29,36} V₁, V₂, V₄, and V₅ are tetrahedrally coordinated species, and V₁₀ is octahedrally coordinated. Also, the vertical scales of the two spectra in Fig. 1 have been adjusted so that peaks in both spectra can be observed. As a result,

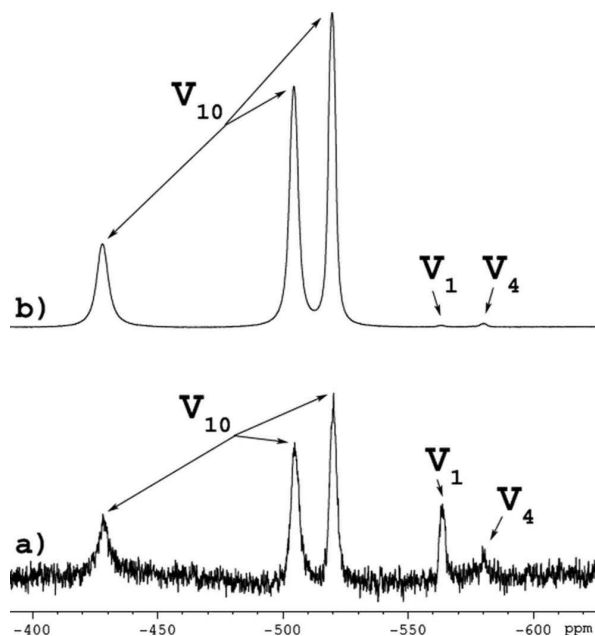


Figure 1. NMR spectra of pH 5.1 0.5 M NaCl solutions with (a) 0.0025 and (b) 0.25 M NaVO₃. The dilute NaVO₃ solution has a greater proportion of tetrahedrally coordinated species (V₁ and V₄) relative to octahedrally coordinated species (V₁₀) compared to the more-concentrated NaVO₃ solution, which contains mostly octahedrally coordinated species.

the two spectra cannot be compared quantitatively. However, the data do show that the 0.0025 M NaVO₃ solution has a greater proportion of tetrahedral species relative to octahedral species compared to the 0.25 M NaVO₃ solution, which contains significantly more octahedral species than tetrahedral species.

Figure 2 shows cathodic polarization curves on Al 2024-T3 in aerated pH 5.1 0.5 M NaCl with 0.25 and 0.0025 M NaVO₃ and without NaVO₃. These experiments show the inverse relationship between NaVO₃ concentration and inhibition of cathodic kinetics at pH 5.1, where the dilute solutions containing relatively more tetrahedrally coordinated vanadate to octahedral vanadates have a larger reduction in cathodic kinetics than more-concentrated solutions with relatively more octahedrally coordinated decavanadate.

Tetrahedral vanadate species in alkaline electrolytes.— Small changes in solution pH can have a large effect on vanadate speciation. Concerns that the vanadate test solutions would change over the course of microcell experimentation, with consequences for inhibitor behavior, were addressed using NMR. Figure 3 shows the spectra from two samples of pH 9.17 0.5 M NaCl + 10 mM NaVO₃ test solution taken immediately before microcell experimentation and 10 days later after the conclusion of experimentation in vanadate solutions. The solution did remain stable over the course of experimentation and was found to contain a number of different tetrahedral vanadate species as expected from previous work on vanadate inhibition.^{18,22} The assignments of V₄ and V₅ are not certain, as two different standards available in the literature leave room for speculative interpretation.^{26,36} However, definitive assignment of these species is not critical for this work. The solution used for this work contained tetrahedrally coordinated species and predominately V₁; no octahedrally coordinated vanadates were detected.

Polarization of intermetallics in tetrahedral vanadate solutions.— Figures 4a-g show sample anodic polarization curves for pure Al, pure Cu, Al 4% Cu, Al₂Cu, Al₂CuMg, Al₇Cu₂Fe, and Al₂₀Cu₂Mn₃, respectively. The objective of these experiments was to determine the effect of tetrahedral vanadates on the anodic behav-

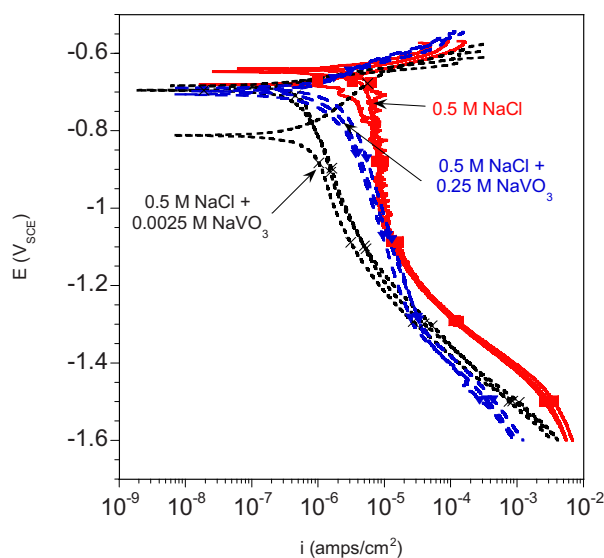


Figure 2. (Color online) Cathodic polarization curves on Al 2024-T3 in aerated pH 5.1 0.5 M NaCl with 0.25 and 0.0025 M NaVO₃ and without NaVO₃. These experiments show an inverse relationship between NaVO₃ concentration and inhibition of cathodic kinetics at pH 5.1, which correlates well with a transition from solutions dominated by octahedrally coordinated vanadates to tetrahedral vanadates.

ior of different constituent intermetallic particles in Al 2024-T3. Detailed anodic polarization results are discussed below in conjunction with cathodic polarization results for each intermetallic.

Figures 5a-g are a collection of cumulative distribution plots showing E_{corr} , E_{pit} , and E_{rp} for various intermetallic compounds. E_{corr} is the corrosion potential, E_{pit} is the pitting potential, and E_{rp} is the reversible potential on the reverse scan, which was defined as the potential at the smallest observed current on the reverse scan. Cumulative probability plots are of value because there can be significant variation in the measured characteristic potentials of intermetallic compounds. Knowing this variation is important in the interpretation of corrosion processes. The statistical variation, which would be lost by simply taking averages, can be shown fully in cumulative distribution plots. The corrosion rate was estimated from both anodic and cathodic polarization curves (to be presented later) by extrapolation of linear passive regions and regions of oxygen reduction, respectively, to the intersection with corrosion potential.

Figures 6a-g show sample cathodic polarization curves for pure Al, pure Cu, Al 4% Cu, Al₂Cu, Al₂CuMg, Al₇Cu₂Fe, and Al₂₀Cu₂Mn₃, respectively. These experiments were used to determine the effect of vanadates on cathodic kinetics of intermetallic particles in Al 2024-T3.

Figures 7a-g are a collection of cumulative distribution plots showing corrosion current density (i_{corr}), passivation current density (i_{pass}), and current density at $-1.3 V_{\text{SCE}}$ for tested intermetallics and metals. Passivation current density was defined as the current density immediately before breakdown. The current density at $-1.3 V_{\text{SCE}}$ was used as a comparative measure of cathodic reduction kinetics, because the potential at this point was below the most active E_{corr} and this point of the curve allowed a direct comparison of reduction kinetics at potentials where oxygen reduction reactions likely contributed to the cathodic response. Considerable hydrogen evolution reactions may also be present at $-1.3 V_{\text{SCE}}$. The following presents results for each tested material.

Pure Al.— The addition of 10 mM NaVO₃ to alkaline 0.5 M NaCl results in a shift of corrosion potential to more active potentials relative to NaVO₃-free solutions on pure Al. However, NaVO₃

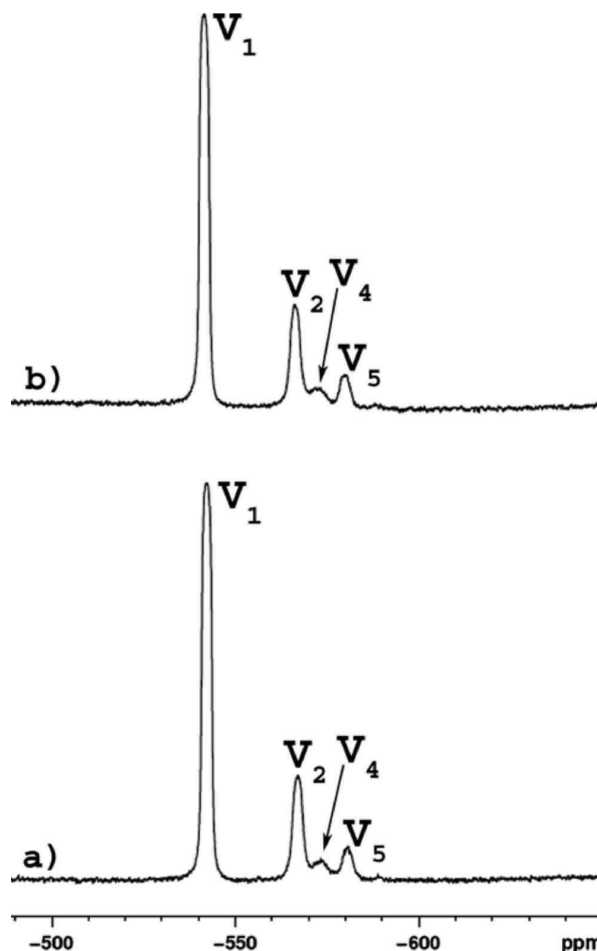


Figure 3. NMR spectra showing the presence of tetrahedrally coordinated vanadates (V_1 , V_2 , V_4 , and V_5) in pH 9.17 0.5 M NaCl + 10 mM NaVO₃ solution used for microcapillary electrochemical experiments (a) immediately prior to experimentation and (b) 10 days later after completion of experiments.

also appears to slightly increase the corrosion current density. A small decrease in cathodic kinetics, as seen by a decrease in current density at $-1.3 V_{\text{SCE}}$ in vanadate solutions, is largely offset by an increase in anodic kinetics, as seen by an increase in i_{pass} observed in NaVO₃ solutions. NaVO₃ increases the breakdown potential of pure Al and does not appear to have an effect on the repassivation potential on the reverse scan.

Pure Cu.— NaVO₃ was observed to have little effect on the corrosion potential, corrosion current density, or repassivation potential on the reverse scan of pure Cu. Pure Cu did not demonstrate passive behavior with an observable characteristic breakdown. However, NaVO₃ was observed to have an effect on dissolution kinetics. Comparison of current density at $-1.3 V_{\text{SCE}}$ shows that NaVO₃ solutions slowed cathodic kinetics.

Al 4% Cu.— Al 4% Cu was used as an analog material for the matrix of Al 2024-T3. NaVO₃ was observed to shift the corrosion potential to more active potentials, and the corrosion current density was observed to decrease as a result of a decrease in cathodic kinetics. A relatively small increase in E_{pit} was observed in NaVO₃ solutions compared to increases observed on other intermetallic compounds. Vanadate increased the current density observed in the passive region of the anodic polarization scans.

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