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Full Length Article

Effects of sulfate and nitrate anions on aluminum corrosion in slightly alkaline solution

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ABSTRACT

The corrosion mechanisms and kinetics of AA1085 in Li_2SO_4 and $LiNO_3$ aqueous rechargeable lithium-ion battery electrolytes were investigated at pH 11 using chronoamperometry. The corrosion kinetics of AA1085 is controlled by the electrolyte concentration level and the anodic potentials. AA1085 is susceptible to crystallographic pitting corrosion in Li_2SO_4 electrolytes. The rates of pit nucleation and pit growth both decreased at higher Li_2SO_4 concentrations or at lower anodic potentials. AA1085 passivates against pitting corrosion in $LiNO_3$ electrolytes due to the formation of a thick, uniform corrosion product layer. The growth rate of the passive film was slightly enhanced by increasing the electrolyte concentration and anodic potentials. X-ray photoelectron spectroscopy spectra showed the formation of a thin sulfate-incorporated passive film on the electrode, which comprises $Al_2(SO)_418H_2O$, $Al(OH)SO_4$ and $Al(OH)_3$, before the occurrence of pitting growth in 2 M Li_2SO_4 electrolyte. The thick corrosion product layer formed in 5 M $LiNO_3$ electrolyte was composed of $Al(OH)_3$ and AlOOH. Raman spectroscopy on deionized water, LiOH solution, Li_2SO_4 and $LiNO_3$ electrolytes depicted changes of solution structure with increasing electrolyte concentration. The influence of extrinsic and intrinsic factors on the corrosion kinetics of AA1085 in Li_2SO_4 and $LiNO_3$ electrolytes at pH 11 are discussed in detail.

1. Introduction

Aluminum finds a wide range of applications due to its distinct properties such as low density, high energy density and considerable corrosion resistance. Investigating the mechanism and the kinetics of aluminum corrosion, especially the localized corrosion of aluminum, is of interest because the corrosion often leads to sudden failure or impairs the function of the component. In lithium-ion batteries, commercial purity AA1085 is widely used as a current collector material [1] and so is of particular interest. Corrosion of the aluminum current collector irreversibly increases the internal battery resistance, contaminates electrolyte, attacks the electrode material and consequently degrades the battery performance, life and even safety [2–4]. The recently developed aqueous rechargeable lithium-ion battery (ARLB) technology has raised concerns with the risk of current collector corrosion in aqueous battery electrolytes. To ensure the chemical stability of specific cathode active materials, the electrolytes of ARLB are usually adjusted to slightly alkaline conditions which are beyond the stability window of aluminum (pH 4–8) as predicated by the Pourbaix diagram [5]. Prior work identified 2 M Li_2SO_4 and 5 M $LiNO_3$ aqueous solutions as high performing ARLB electrolytes [6]. The highly concentrated salt solutions add more complexities to the stability of aluminum in ARLB systems.

Attempts have been made to understand the effects of sulfate and nitrate anions on the corrosion of high-purity aluminum, but there are some discrepancies in the literature. Poggi et al. claimed that addition of 0.01 to 0.1 M SO_4^{2-} mitigates the corrosion of high-purity aluminum in slightly alkaline solutions by a competitive adsorption mechanism [7]. It was claimed that the sulfate anions significantly retard the crystallization of gibbsite from amorphous aluminum oxide in aqueous solutions [8]. Using electrochemical noise analysis, Na and Pyun described that the presence of SO_4^{2-} and NO_3^- enhances the corrosion of high-purity aluminum in aqueous alkaline solution [9]. Branzoi reported that addition of 0.05 M and 0.1 M hydroxyl anions in 1 M $NaNO_3$ solution leads to extensive localized attack on high-purity aluminum [10]. While it was also claimed that nitrate combining with other inorganic anions effectively inhibits aluminum corrosion in alkaline solutions [11]. To the best of our knowledge, no literature has described the effects of SO_4^{2-} and NO_3^- on the corrosion of commercial purity aluminum in slightly alkaline solutions and so the corrosion kinetics of this common aluminum current collector alloy in slightly

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alkaline ARLB electrolytes is not clear. The highly concentrated Li_2SO_4 and $LiNO_3$ electrolytes used in ARLB, which provide desirable stability of a lithium anode and high ionic conductivity of the electrolyte, may intensify the effects of sulfate and nitrate anions on aluminum corrosion. Yamada et al. reported that highly concentrated LiFSA-based electrolytes effectively suppress aluminum corrosion up to 4.5 V versus Li^+/Li [12]. The inhibiting effect of the concentrated electrolytes was explained by the declined activity of free solvent molecules. Understanding the relationship between the electrochemical stability of aluminum and the structure of concentrated aqueous electrolytes may help explain the role of SO_4^{2-} and NO_3^- on aluminum corrosion. The purpose of the present work is to describe the influence of sulfate and nitrate anions on the corrosion kinetics of AA1085 in slightly alkaline solutions relevant to ARLB conditions. This will support corrosion management in the design of aqueous based energy storage systems and the extensive use of aluminum and aluminum alloys in many other industrial applications where exposure to similar conditions may occur.

2. Materials and methods

2.1. ARLB electrolyte

The aqueous electrolytes were prepared by dissolving specific weights of LiOH (anhydrous, 98%, Alfa Aesar) in de-ionized water to adjust the pH to 11, followed by addition of lithium salts to target concentration of 0.1 M, 0.5 M and 2 M Li_2SO_4 (anhydrous, 99.7%, Alfa Aesar) and 0.1 M, 2 M and 5 M $LiNO_3$ (anhydrous, 99.98%, Alfa Aesar) equivalent. These target compositions were based on the optimal electrolyte compositions with additional iterations at lower concentrations [5]. The solutions were magnetically stirred until the salts were fully dissolved and the pH was again adjusted to 11 with LiOH. The pH value was monitored using a Mettler FE20 Ag/AgCl pH electrode.

2.2. Electrochemical tests

Electrochemical tests were conducted using PARSTAT-4000 in a conventional three-electrode plate material evaluating cell (BioLogic Science Instruments) that allows a constant electrode area of 0.5 cm^2. Ag/AgCl with saturated KCl solution (0.197 V vs SHE) was used as the reference electrode. The reference electrode was separated from the body of the cell using a Luggin capillary to minimize the IR drop. A platinum wire with surface area of approximately 1 cm^2 was used as the counter electrode. The stability window of each prepared aqueous electrolyte solution was determined by performing linear sweep voltammetry on high purity platinum foil scanned from open circuit potential either to the anodic or the cathodic direction with a scanning rate of 1 mV/s until significant gas evolution occurred. The platinum foil and the platinum counter electrode were cleaned with dilute nitric acid, rinsed with distilled water and air dried before each measurement. As-received AA1085 foil of thickness 20 μm was rinsed with isopropyl alcohol, acetone and air-dried prior to testing. The composition of AA1085 is presented in Table 1. The open circuit potential (OCP) of AA1085 was measured in each aqueous electrolyte after stabilization for 2.5 h. Chronoamperometry was carried out on fresh AA1085 foil in aqueous electrolytes at an anodic potential for a period of 24 h. The anodic potential is selected below the positive vertex of the stability window of the aqueous electrolytes and corresponds to high operating voltage conditions in ARLB. After the electrochemical tests, the aluminum electrode was immediately removed from the cell, gently rinsed with DI water and dried using a gentle stream of nitrogen for subsequent characterization. Each test was performed at least three times and the representative data are reported. All potentials values in this paper are reported in the Ag/AgCl, saturated KCl (0.197 V vs SHE) scale.

2.3. Surface characterization

The surface morphology of the electrodes after choronoamperometry was examined with a Hitachi S-4800 scanning electron microscope. X-ray photoelectron spectroscopy (XPS) was performed using a Perkin Elmer 5440 X-ray Photoelectron Spectrometer with Mg Kα source. The AA1085 electrode surface was sputtered by Ar^+ ion over an area of 4 mm^2 to analyze the chemical state of the passive film through the depth direction. XPS spectra were recorded after the passive film was sputtered by Ar^+ ion for 0, 5, 10, 15, 20 and 25 min. The XPS etching rate was determined to be 1 nm/min using an alumina film of known thickness grown on a silicon wafer surface using atomic layer deposition. The carbon 1 s peak with a binding energy of 284.6 eV was used as the reference for spectrum calibration. The core level peaks were analyzed using a Tougaard-type background. The peak positions and areas were optimized using a weighted least squares fitting method with 80% Gaussian, 20% Lorentzian line shapes. Raman spectroscopy was performed using a Renishaw Inc. 1000B with a helium-neon laser producing highly polarized light at 633 nm with power at the sample of 10 mW. Raman spectra were collected in the range of 200 and 4000 cm^{-1} and calibrated using the 519.5 cm^{-1} Si peak from a silicon wafer reference. All measurements were taken with a 10 s integration time and with fixed parameters of the instrument to ensure a constant response function.

3. Results and analysis

3.1. Stability window of solutions measured by LSV

The operating voltage range of ARLB is confined to the stability window of the electrolyte. The theoretical gas evolution potentials can be calculated from thermodynamic principles as $E_{H^+/H_2} = -0.059pH$ and $E_{O_2/H_2O} = 1.23 - 0.059pH$, where E_{H^+/H_2} is the hydrogen evolution potential and E_{O_2/H_2O} is the oxygen onset potential. At pH 11, the theoretical stability window of ARLB electrolyte is 1.23 V and exists between −0.846 V and 0.384 V vs Ag/AgCl (sat'd KCl) reference electrode. The stability windows were measured experimentally by carrying out linear sweep voltammetry on a platinum foil in each test solution at pH 11. E_H and E_O, which denote the measured onset potential of hydrogen and oxygen evolution of aqueous solutions, respectively, were obtained and are presented in Table 2. The results show that the concentrated aqueous electrolytes reduce water activity and extend the stability windows beyond the theoretical value of the pure aqueous condition, which is possibly due to kinetic barrier effects at elevated salt concentrations [13].

Table 1
Composition of AA1085 current collectors used in lithium ion batteries.

Grade	Composition specification (maximum values, in wt.%)								
AA1085	Si 0.1	Fe 0.1	Cu 0.03	Mg 0.02	Zn 0.02	Ga 0.03	V 0.05	Other (each) 0.01	Al (minimum) 99.85