



# Corrosion and electrochemical evaluation of an Al–Si–Cu aluminum alloy in ethanol solutions

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## ABSTRACT

The corrosion of aluminum alloy AlSi8Cu3Fe(Zn) in ethanol and ethanol solutions containing 10 vol.% water and 10 vol.% acetic acid, respectively, was investigated by means of electrochemical impedance spectroscopy (EIS), polarization curve, immersion, optical microscopy, scanning electron microscopy and element mapping. The Al alloy in the ethanol and its solutions exhibited a capacitive loop in the measured Nyquist EIS spectra at high frequencies, which can be attributed to the ethanol's dielectric response. Addition of 10 vol.% acetic acid increased the ethanol corrosivity more significantly than the same amount of water addition. The Al–Si–Cu–Mg precipitated zones in the alloy were susceptible to corrosion attack due to the micro-galvanic effect by the Cu-containing precipitates.

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## 1. Introduction

With the increasing concern of sustainability and pollution of fossil fuel, renewable and clean-burning natural biofuel is an important supplement to the traditional petrol. Ethanol is an important component of biofuel [1]. In the past decade ethanol production has increased significantly. For example, in 2000 the world ethanol output was 16.9 billion liters, while in 2009 this figure became 72.0 billion liters [2]. In USA, the federal requirement for a minimum usage of biofuel also increases every year [3]. It is expected that ethanol will become an essential fuel in future.

In the auto industry, E85 fuel currently available in North America contains about 85 vol.% ethanol [4]. However, ethanol is not compatible with Al [5–8]. Unfortunately, aluminum alloys are important automotive structural materials. There is a concern that high ethanol content biofuels may attack Al components. However, investigations on ethanol-related Al corrosion are rarely reported. There are only a few publications on corrosion of Al in some mixtures that contain ethanol, fuels and chloride salts [5–11]. For example, Heitz et al. [12–15] extensively investigated the corrosion and passivation of metals in organic solvents, including ethanolic solutions. Their work led to an understanding that the corrosion in organic solvents follows electrochemical mechanisms analog to those in aqueous solutions. However, their research

interest was mainly in the influence of various additives on corrosion of metals in organic solvents. There is relatively limited information on corrosion of Al alloys in ethanol in their publications. So far, the effect of ethanol without mixing with other chemicals on the corrosion of Al alloys has not been thoroughly studied.

In biofuel studies, researchers are more interested in dry corrosion of Al at temperatures above the ethanol boiling temperature (~78 °C) [5,6,10,16,17]. The possible corrosion attack at a relatively low temperature is usually overlooked, and thus has not been carefully investigated. In practice, automotive parts are more often exposed to ethanol-containing fuels at temperatures below the fuel boiling points. For example, the fuel pipeline normally operates at room temperature. Even in an engine block, when a car is parking, the temperature is also far below the ethanol boiling temperature. For a passage car, its overall parking time is usually longer than its overall running time. The room temperature corrosion performance of its engine block material should also have a significant contribution to the engine's service life. Therefore, it is essential to understand the corrosion behavior of Al alloys in ethanol at temperatures below the ethanol boiling point.

Among the Al alloys that may be attacked by ethanol in the auto industry, the 3xx series of Al–Si–Cu alloys have satisfactory mechanical and high temperature creep properties. They are normally used for engine blocks/heads, fuel pumps and delivery pipes that are in direct contact with ethanol fuel in service. As the alloys have complicated intermetallic phases, it would be of scientific interest to understand the influence of microstructure on corrosion for these alloys in ethanol.

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Compared with conventional aqueous electrolytes, ethanol has very low electrical conductivity [18]. There is difficulty in employing traditional electrochemical techniques to investigate the corrosion mechanism of Al in ethanol. To make use of electrochemical methods, some supporting electrolyte additives have been considered, such as perchlorate salts [8]. However, this brings up a question whether the corrosion mechanism of Al is altered by the additives [19]. It would be advantageous if an electrochemical approach could be established to investigate the ethanol-induced corrosion without addition of supporting electrolyte additives.

In this study, the ethanol-induced corrosion of AlSi8Cu3Fe(Zn), a typical Al–Si–Cu Al alloy, below the ethanol boiling temperature was investigated. The primary aim of this study is to understand the corrosion mechanism of the Al alloy in ethanol and its solutions under ambient conditions. In addition, establishment of a successful electrochemical impedance spectroscopy (EIS) technique for investigating ethanol–Al corrosion systems is also pursued in this study.

## 2. Experimental

### 2.1. Al alloy sample and ethanol electrolytes

As-cast AlSi8Cu3Fe(Zn) alloy (7.74 wt.% Si, 3.23 wt.% Cu, 0.99 wt.% Fe, 0.16 wt.% Ni, 0.27 wt.% Mn, 0.10 wt.% Mg, 1.28 wt.% Zn) coupons (2 cm × 2 cm × 2 cm) were abraded with SiC paper and then polished with diamond paste through 0.05 μm grit. Alcohol (94.0–96.0 wt.% ethanol, 4.0–6.0 wt.% isopropyl alcohol, <0.05 wt.% water) purchased from VWR chemical company was used as an “anhydrous” ethanol in this study. This ethanol might contain a very small amount (<0.05 wt.%) of water. As it was carefully handled similarly in all the experiments, the systematic error resulting from the low water content should not affect the discussion and final conclusions in this study.

To understand the influences of water and acetic acid on the corrosivity of ethanol, de-ionized water and acetic acid were added in the “anhydrous” ethanol to make up water blended and acetic acid blended ethanol electrolytes/solutions. These blended ethanol solutions contain 10 vol.% acetic acid and 10 vol.% water (volume ratios of ethanol:acetic acid = 9:1 and ethanol:water = 9:1), respectively.

### 2.2. Electrochemical impedance spectrum and polarization curve measurements

AC impedance spectra of the Al alloy were measured at its open circuit potential (OCP) after 6 h of immersion in an EG&G flat electrolyte cell containing ethanol or the ethanol solution containing 10 vol.% water or 10 vol.% acetic acid by using a Modulab system (Solartron Analytical). During measurements, the HV 100 high voltage module of the Modulab was selected considering the low electrical conductivity of ethanol. In the cylindrical flat electrolyte cell (the inner diameter ~10 cm), the counter electrode was a platinum gauze, and a KCl saturated Ag/AgCl reference electrode was placed in front of the working electrode, about 2 mm away from its surface. Only 1 cm<sup>2</sup> of the Al alloy working electrode surface area was exposed to the electrolyte in the cell. AC frequency range was set from 17,777 Hz to 0.01 Hz. Due to the low electrical conductivity of ethanol, a large portion of the applied potential perturbation will drop in the ethanol electrolyte, which cannot trigger a reliable current response across the Al alloy/ethanol interface. Thus, a relatively large amplitude (30 mV peak-to-peak) of AC stimulating potential was applied. As the Al alloy electrode has a linear current response in a wide potential region around the OCP according to its polarization curve measurements, it can still

be treated as a linear system for AC EIS analysis under this amplitude of AC potential stimulation.

After EIS measurements, potentiodynamic polarization curves of the Al alloy in the solutions were conducted by scanning polarization potential from –0.7 V to 0.7 V (vs. OCP) at 10 mV/min.

All the EIS and polarization curve measurements were performed at 25 °C.

### 2.3. Electrolyte resistance measurement

To verify the solution impedance (resistance) involved in a measured AC impedance spectrum, three specially designed electrolyte cells made of plastic funnels with different funnel “tail” lengths (6 cm, 8 cm and 10 cm) as illustrated in Fig. 1 were used. The surface area of the working electrode exposed to the electrolyte in these funnels was around 1.3 cm<sup>2</sup>; the distance between the Al alloy working electrode and the reference electrode was determined by the funnel “tail” length. EISs in high frequency range 17,777–450 Hz (scanning from high frequency to low frequency and the scanning could be stopped at a frequency prior to 450 Hz when a satisfactory capacitive loop in Nyquist plane was obtained) were measured with these funnel cells at room temperature.

### 2.4. Immersion test

Immersion tests were carried out in capped glass bottles containing 30 mL of ethanol for 25 days. To ensure detectable corrosion damage within 1 month, the testing temperature was controlled at 70 °C in a water bath. The bottles were sealed with Parafilm to minimize the absorption of moisture from air during test.

### 2.5. Metallographic observation and SEM analysis

The optical microscopic images of the Al alloy before and after immersion (rinsing with water and drying in air) were recorded under a Leica Reichert MEF4 optical microscope to show the alloy

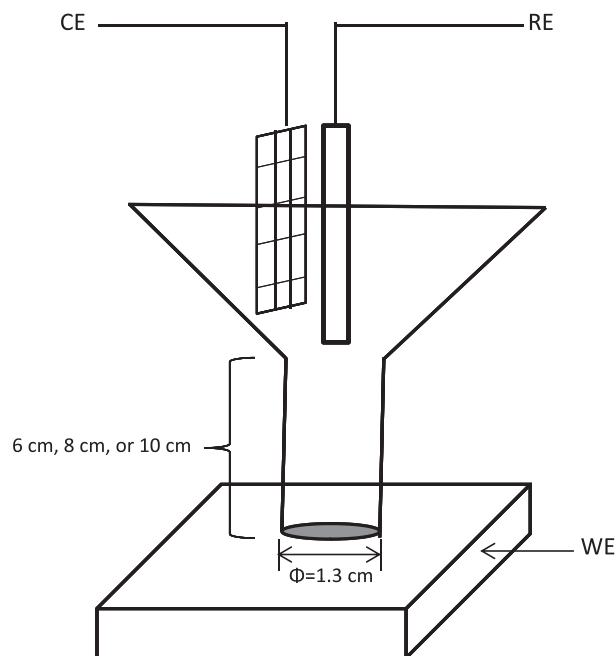


Fig. 1. Schematic illustration of the set-up for ethanol impedance measurement with a reference electrode together with a Pt gauze being placed at different distances from the Al alloy surface.

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