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Corrosion behavior of surface treated steel in liquid sodium negative electrode of liquid metal battery

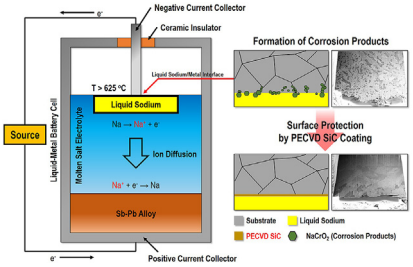
Jeonghyeon Lee [a], Sang Hun Shin [b], Jung Ki Lee [a], Sungyeol Choi [a], Ji Hyun Kim [a, *]

[a] School of Mechanical and Nuclear Engineering, Ulsan National Institute of Science and Technology (UNIST), UNIST-gil 50, Ulsan 689-798, Republic of Korea
[b] Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon 305-353, Republic of Korea

HIGHLIGHTS

- Corrosion behavior of Fe–Cr alloy in liquid metal batteries was investigated.
- EIS was used to measure the oxidation kinetics of Fe–Cr specimen in liquid Na.
- CVD coating of Si compounds can delay corrosion of structural material in liquid Na.
- SiC coating was more durable than Si_3N_4 coating in high-temperature liquid Na.
- Under coating, Cr-rich zone was narrower than that of as-received specimen.

GRAPHICAL ABSTRACT



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ABSTRACT

While liquid metal batteries are attractive options for grid-scale energy storage applications as they have flexible siting capacities and small footprints, the compatibility between structural materials such as current collectors and negative electrode such as sodium is one of major issues for liquid metal batteries. Non-metallic elements such as carbon, oxygen, and nitrogen in the liquid sodium influence the material behaviors of the cell construction materials in the battery system. In this study, the compatibility of structural materials with sodium is investigated in high temperature liquid sodium, and electrochemical impedance spectroscopy (EIS) is used to monitor in-situ the corrosion behavior at the surface of materials in sodium. Chemical vapor deposition (CVD) coatings of SiC and Si_3N_4 are applied as protective barriers against dissolution and corrosion on the steel surface. The results show that CVD coating of Si compounds can delay corrosion of steel in high temperature liquid sodium comparing to the result of as-received specimens, while SiC coating is more durable than Si_3N_4 coating in high temperature liquid sodium.

1. Introduction

Energy storage is a growing global concern and important problem for the future, considering the drastic increases in the price of refined fossil fuels and the environmental consequences of the use of such fuels. The liquid metal battery is a novel battery

* Corresponding author.
E-mail address: kimjh@unist.ac.kr (J.H. Kim).

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system with performance characteristics suitable for deployment as a grid-scale electrochemical energy storage solution with a long lifetime and low cost A liquid metal battery consists of two liquid metal electrodes separated by a molten salt electrolyte; the components self-segregate into these three layers based on the immiscibility and density differences of the materials [1–5]. Liquid metal electrode materials, such as Ni, Na, K, Mg, Ca, Rb, Sr, Cs, Ba, (as negative electrode) and Pb, Bi, Sn, Sb, Te, Tl, Hg, Cd, Zn, etc., (as positive electrode) are constrained according to the following three requirements [1]:

(1) Liquid phase at practical temperatures: the melting temperature must be less than 1000 °C and the boiling point greater than 25 °C
(2) Electrically conductive, with a minimum electronic conductivity exceeding the ionic conductivity of a typical molten salt electrolyte
(3) Nonradioactive and available as a naturally occurring stable isotope

Liquidity endows liquid metal batteries with superior transport properties and kinetics. The operating voltage of any electrochemical cell, E_{cell}, deviates from the equilibrium cell potential, $E_{cell,eq}$, based on losses and voltage inefficiencies η that depend on the current density j such that $E_{cell}(j) = E_{cell,eq} - \sum \eta_i(j)$. Liquid metal batteries have ultrafast electrode charge-transfer kinetics because of the liquid–liquid electrode-electrolyte interfaces, high rate capability, and low ohmic losses enabled by the highly conductive (up to 3 S cm^{-1}) molten salt electrolytes, and the rapid mass transport of reactants and products to and from the electrode-electrolyte interface enabled by liquid-state diffusion [1]. The battery systems have performance characteristics suitable for application as grid-scale electrochemical energy storage devices with long lifetimes and low costs as advantages [1,3].

Despite the advantages conferred by the liquid state, the high operating temperature and strong reactivity of liquid metal battery electrodes can cause the corrosion of the cell construction materials, including those used to fabricate current collectors, containers, insulators, and seals. This is a primary concern for the long-term performance of the battery system. Oxidation of the electrodes can cause chemical depositions on the electrode surface, which can develop an insulating layer that results in irreversible capacity losses. The oxidation can cause gas evolution, which can increase the internal pressure in the cell [6,7].

A wide range of engineering materials, including stainless steels and low-carbon steels, have been identified as compatible with liquid alkali metals, such as sodium [8]. The negative current-collector materials of liquid metal batteries, such as austenitic steels and ferritic/martensitic steels (FMS), are subject to mass-transfer phenomena in liquid sodium [9].

Because they are exposed to the liquid sodium for long periods, the structural materials experience highly corrosive environments. The increased high temperature of the environment may reduce the margins of safety against failure during normal operation, as well as promoting corrosion [10,11]. Therefore, the effects of corrosion-related behavior, such as surface corrosion rates, carburization, and decarburization, on the mechanical properties of the structural materials during the operation of the liquid metal battery must be thoroughly understood.

The mechanical properties of the structural materials may degrade by dissolution, chemical reactions, and carbon transfer in the liquid sodium. Sodium promotes the corrosion of these materials by dissolving the alloy constituents and chemically reacting with impurities, especially oxygen and carbon, located in the sodium environment [12,13]. As such, the compatibility of structural materials with liquid sodium must be carefully investigated.

During the dissolution process, the dissolved constituents near the specimen surface diffuse into the liquid sodium [14–16], because of the difference in chemical activity. A compatibility test of structural materials with sodium revealed that the degradation of the mechanical properties is governed by aging [17].

The material degradation of structural materials is caused by the corrosion of materials in liquid metal batteries. In the materials of corrosion-resistant cell construction, it is required to maintain the mechanical and chemical integrity by preventing the increased resistance and the reduced capacity of battery cell over time [1]. In the lithium ion battery, it is well known that aluminum, used as the cathode current collector, has the severe problem related to corrosion [18,19]. The oxidative dissolution of aluminum occurs through a mechanism initiated by anion attack of the native oxide layer on the surface of the current collector at high potentials (>4.2 V vs. Li/Li^+).

When steel corrodes, chromium as an alloying element is consumed by dissolved oxygen to form ternary oxides, such as $NaCrO_2$. Because of the formation of chromium-containing oxides, chromium is removed from the structural steel, which can cause degradation [20].

In a previous study by Shin et al. [15], austenitic Fe–18%Cr–8%Ni and alpha-iron foils were equilibrated in 550 °C sodium, and the concentration of carbon in the foils was analyzed. An equilibrium method was developed to measure the activity of carbon in the liquid sodium by a new expression. In the study, carbon transfer occurred in the high-temperature liquid sodium. It was found that austenitic steels were corroded by high-temperature liquid sodium. This influenced the performance and the efficiency of the liquid metal batteries.

In this study, chemical vapor deposition (CVD) coatings of SiC and Si_3N_4 on FMS were tested as barriers against corrosion and dissolution. The CVD-coated specimens were used to determine the compatibility of FMS with high-temperature liquid sodium anodes. According to Kano et al. [21], it was reported that SiC and Si_3N_4 had superior properties than other ceramics in high temperature liquid sodium environment. Electrochemical impedance spectroscopy (EIS) was used in a lead-bismuth eutectic (LBE) system to characterize the corrosion kinetics [22]. EIS measurements were taken continuously from one specimen throughout the LBE exposure test. In this study, EIS is used to investigate the corrosion behavior of structural materials by 'in-situ' monitoring in liquid sodium as the anode of a liquid metal battery. The use of EIS to measure the impedance responses of SiC, Si_3N_4, and any oxides that may be present enables the monitoring of FMS corrosion [23,24]. The objective of this study is to investigate the corrosion behavior of structural materials used in liquid sodium anodes using EIS, and to investigate the efficacy of CVD coatings as protective films in this environment.

2. Experimental

2.1. Materials

The chemical composition of the steel used in this study is shown in Table 1. The material is normalized and tempered ASTM A182 Grade 92 steel. The specimens were normalized at 1080 °C for

Table 1
Chemical composition of the test material.

	C	Si	Mn	Cr	Ni	Mo	W	V
Gr.92	0.087	0.21	0.41	8.69	0.13	0.38	1.62	0.18