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Design of Mg–Ni alloys for fast hydrogen generation from seawater and their application in polymer electrolyte membrane fuel cells

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ABSTRACT

Mg and its alloys are very attractive for hydrogen generation via hydrolysis because their hydrolysis reaction occurs in neutral seawater instead of the alkaline water necessary for the hydrolysis of Al and its alloys. The hydrogen generation rate from the hydrolysis of Mg is proportional to the corrosion rate of Mg to Mg^{2+} . Mg powder, though producing a high reaction rate in the hydrolysis, causes explosive dangers when in contact with air or moisture. However, Bulk Mg such as plate and sheet exhibits an extremely low hydrogen generation rate. To overcome the disadvantage, Mg–Ni alloys were designed to form an electrochemically noble phase (Mg_2Ni) along grain boundaries (G.B.), and hence to significantly accelerate the hydrolysis rate by causing a galvanic and intergranular corrosion between the noble Mg_2Ni and Mg matrix. In particular, the Mg–2.7Ni alloy among the designed Mg–Ni alloys exhibits the highest hydrogen generation rate ($23.8 \text{ ml min}^{-1} \text{ g}^{-1}$) that is 1300 times faster than that of pure Mg. Furthermore, it was demonstrated that PEMFC stably produced 7.3 W for 20 min when it is operated by the hydrogen generated from the hydrolysis of 2 g Mg–2.7Ni alloy, that is, equivalent to 1.215 KWh/Kg-Mg–2.7Ni alloy.

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Introduction

Hydrogen energy, which features numerous benefits, including abundant, environmentally friendly properties and high energy density, is an excellent candidate for future energy source [1,2]. Chemical hydrogen energy can be converted to electrical energy by a fuel cell or an electrochemical energy conversion device. Among the numerous types of fuel cells,

polymer exchange membrane fuel cells (PEMFCs) have received great attention due to their low operating temperature, high power density, and variety of applications [3,4]. Most of the hydrogen provided to the anode side of a PEMFC is produced by steam or partial oxidation reforming of natural gas and coal gasification. However, these materials cause CO_2 emission problems due primarily to the use of fossil fuels. The extraction of hydrogen from the hydrolysis of electrochemically active metals such as Al [5–15], Mg [16–19], and Zn [20]

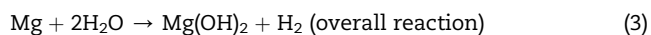
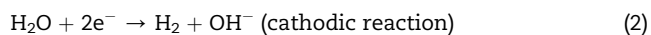
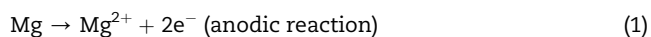
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has received great attention because this process eliminates the need for hydrogen storage and does not emit environmental pollutants [11–14]. In addition, these active metals are abundant and cheap. The hydrogen generation rate from the hydrolysis of the active metals is easily controllable based on the reaction area of active metals. Among the active metals, Al and Al alloys have been studied by numerous researchers because of their high H₂ storage densities in water (Al: 3.7 wt.% H₂; Mg: 3.3 wt.% H₂) [5–14]. However, the hydrogen generation from the hydrolysis of Al has a limitation due primarily to the fact that the process occurs only in strong alkaline water (pH ≥ 14). In contrast, the hydrolysis reaction of Mg and its alloys occur in neutral aqueous solutions that contain chloride ions, such as seawater [16–19]. In addition, Mg offers many advantages as a raw material for hydrogen generation, including high reactivity (−2.37 V_{SHE}), low density (1.74 g/cm³), abundance (Mg is the sixth-most abundant element on Earth), and low cost (bulk Mg: \$3/kg) [21]. The chemical reactions for hydrolysis of Mg in an aqueous solution can be expressed by Eqs. (1)–(3) [18,19,21,22]:



With hydrolysis of Mg, the solution is gradually alkalized by reaction (2). When the pH increases to a value greater than 10.2, the hydrolysis reaction of Mg is rapidly retarded by the formation of a passive Mg(OH)₂ layer on the Mg surface. The Mg hydroxide layer is easily destroyed due to the pitting corrosion caused by the chemical attack of Cl[−] ions [21–24]. Thus, hydrogen generation from the hydrolysis reaction of Mg easily and conveniently occur in seawater. Many studies have utilized Mg powders as raw materials for hydrogen generation because of their high reaction area [25,26]. Even though Mg powder has a high H₂ generation rate; it is dangerous when in contact with moisture and heat. Furthermore, Mg powder is relatively expensive due to its complex manufacturing process. The production of hydrogen from bulk Mg has been investigated [27–29]. However, Bulk Mg such as plate and sheet, though being cheap and safe, exhibits an extremely low hydrogen generation rate that is insufficient for commercialization. Accordingly, development of cheap and safe Mg and Mg alloys with high hydrogen generation rates has proven challenging. The rate of hydrogen production from the hydrolysis of Mg is proportional to its corrosion or oxidation rate in water, in accordance with Eq. (1). Consequently, to increase the hydrogen generation rate from the hydrolysis of Mg, the corrosion rate of Mg should be increased. One strategy for increasing the corrosion rate is to precipitate an electrochemical noble phase along the grain boundaries, and hence to cause a galvanic corrosion between the noble phase and the matrix Mg phase. Ni deleteriously reduces the corrosion resistance of Mg alloys and is one suitable alloying element for achieving a fast hydrolysis reaction of Mg [21]. On the basis of

the Mg–Ni binary phase diagram, an additive Ni element forms an intermetallic compound (Mg₂Ni) with Mg whose electrochemical potential is more noble to that of Mg. Accordingly, the hydrogen production rate from the hydrolysis of Mg–Ni alloys in seawater would be accelerated by the combined action of galvanic and intergranular corrosion that is caused by Mg₂Ni coupled to Mg matrix phase.

In this work, Mg alloys containing small amounts of Ni were designed to form a phase (Mg₂Ni) along the grain boundaries that is electrochemically more noble than pure Mg. The effects of the Ni content on the microstructure of Mg alloys and hydrogen production kinetics from the hydrolysis of Mg in seawater (3.5wt.% NaCl) was investigated. Furthermore, the feasibility of using the hydrolysis of Mg–Ni alloys in seawater as a hydrogen source for PEMFCs was examined.

Experimental

Preparation of materials

Mg–Ni alloys were prepared from pure Mg (99.9%) and pure Ni (99.9%). To produce Mg-x wt.% Ni alloys (x = 0.5–2.7 wt.%), Mg and Ni, weighed according to alloying content, were mixed and melted in a carbon crucible at 650 °C for 3 h under protective gas (CO₂, SF₆) because of the explosiveness of fused Mg when in contact with moisture. To remove moisture from a mold made of stainless steel, the mold was heated for 20 min at 350 °C. Afterwards, the fused Mg alloy was poured into the mold and was allowed to air-cool. The specimen of hydrogen generation test was cut into rectangular parallelepiped shapes of 1 × 1 × 0.1 cm³. Mg₂Ni alloy (Mg-53wt.% Ni) was also prepared to confirm galvanic corrosion behavior between matrix phase (Mg) and electrochemically noble phase (Mg₂Ni) in the same way as mentioned above.

Analysis of physical and electrochemical properties

The surface morphology, chemical composition, and micro-phase structure of the Mg–Ni alloys were analyzed using scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS) with atomic mapping, and X-ray diffraction (XRD). Polarization curves of the pure Mg and Mg₂Ni alloys, respectively, were measured in 3.5 wt.% NaCl solution at 25 °C with a scan rate of 1 mV/s. The electrochemical cell equipped with a platinum counter electrode, a saturated calomel reference electrode (SCE), and working electrode (exposed area: 0.1256 cm²) were used for the polarization tests. Galvanic coupled current between Mg and Mg₂Ni was measured in 3.5 wt.% NaCl solution at 25 °C by a zero resistance ammeter (ZRA) that is electrically connected between Mg₂Ni cathode and Mg anode with their distance being 0.5 cm. The exposed areas (area ratio of anode: cathode = 11.5:1) of Mg and Mg₂Ni were 0.1256 cm² and 0.01 cm², respectively.

Measurement of the hydrogen generation rate

Hydrogen generation from the hydrolysis of Mg–Ni alloys was performed in 75 ml of 3.5 wt.% NaCl solution at 25 °C–70 °C. The reactor was immersed in a water bath to stabilize the

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