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Effect of adding cerium to lithium on the performance of discharge and hydrogen evolution of the lithium anode

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ABSTRACT

The effect of cerium as an inhibitor on the discharge and hydrogen evolution at a lithium anode in alkaline electrolyte with additives was evaluated. The electrochemical behaviors of lithium and lithium–cerium alloy are assessed by hydrogen evolution collection, discharge current density, anodic potential, XRD (X-ray diffraction) and scanning electron microscope (SEM). For these conditions, the results show that minor addition of cerium to lithium decreased the hydrogen evolution on the surface of lithium–cerium alloy in an alkaline electrolyte containing corrosion inhibitors. SEM and XRD observation showed that the slow dissolution of lithium–cerium alloy generates the formation of LiOH, $LiOH \cdot H_2O$ and $Ce(OH)_3$. The lithium–cerium surface is less porous than the lithium surface. Hydrogen evolution decrease, prompted by adding cerium to lithium, which is related to reduced porosity of the film enhanced by $Ce(OH)_3$.

1. Introduction

Lithium has high specific energy and high specific power. The theoretical specific energy of the lithium is 11,148 Wh kg^{-1} based on the Li/O_2 reaction, or 8450 Wh kg^{-1} based on the Li/H_2O reaction. It is an attractive material for energy applications due to its negative standard electrochemical potential ($-3.05\ V_{SHE}$) and high unit mass electrochemical equivalence (3.86 Ah g^{-1}). A lithium–water system is very appealing from the specific energy viewpoint [1]. In this system, lithium is used as negative electrode and the positive electrode is a kind of material with less hydrogen over-potential including nickel or stainless steel. When they are submerged in aqueous solution and connected with wire outside, the current occurs through the wire. This was observed using an amperometer. However, a disadvantage to using lithium in lithium–water system arises from its parasitic reaction with water. As a result, the practical energy density and current efficiency of lithium decrease. Study on the electrochemical behaviors of lithium in alkaline aqueous solutions and how to decrease the hydrogen evolution rate has been conducted by several research groups [1–5]. Initial studies focused on the electrolyte additives expected to reduce the activity of water, or modify the interface property [3,6]. In these studies, lithium was exposed to alkaline solutions. Other investigations have focused on the protected film on the lithium anode [7–10]. In these studies, the lithium surface was separated from aqueous solution and the current efficiency was enhanced with low current density. Alloying lithium with another metal element is also an important part of the efforts to develop a highly efficient lithium–water battery. In this effort, alloying the lithium anode with aluminum has been investigated. It is reported that the hydrogen evolution rate was reduced at the lithium–aluminum anode surface [11,12]. However, the anodic efficiency suffered losses concomitant to inordinately low current density due to higher aluminum content in the anode. In general, the literature on alloying lithium with other metal elements is limited. During previous research, this group found that minor addition of magnesium or calcium to lithium altered the lithium surface film by forming alkaline earth metal hydride or hydroxide [13–15]. Cerium is a rare earth metal with a comparatively negative standard electrochemical potential [−2.480 V vs. standard hydrogen electrode (SHE)]. Pauling's cerium electro-negativity is near that of lithium. The Li–Ce phase diagram is shown in Fig. 1. In this system, the solid solution of cerium in lithium is minor [16]. The solubility of cerium hydroxide formed from cerium in contact with alkaline aqueous solution is comparatively lower and more stable than that of lithium hydroxide, magnesium hydroxide, and calcium hydroxide, respectively [17]. In the present paper, a minor amount of cerium was added to the lithium anode as an alloying element and its effects on the discharge and hydrogen evolution at the lithium anode in 4 M (mol L^{-1}) alkaline solutions with some additives were investigated. The surfaces of the lithium and lithium–cerium alloy were subsequently observed by SEM and XRD analysis.

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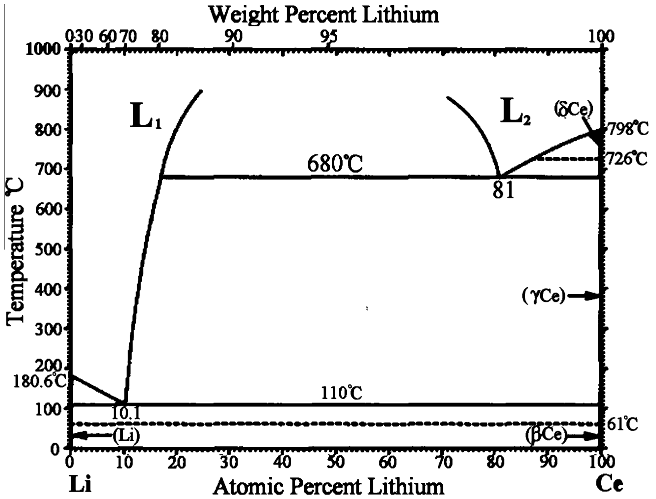

Fig. 1. The phase diagram of Li–Ce alloy [15].

2. Experimental

The experiments of discharge current and hydrogen evolution rate were performed utilizing the setup shown in Fig. 2. Lithium metal bars (99.95%, 15 mm thick and 100 mm long, China JianZhong Nuclear Fuel Co. Ltd.) and cerium metal ingot (99.9%) were used to prepare the lithium–cerium alloy. Lithium–cerium alloy (Li–0.08 wt.% Ce) was prepared in a resistance furnace using a stainless steel crucible in a dry argon atmosphere. The controlled smelting temperature ranged 800–1000 °C. The lithium and lithium–cerium alloy ingots were precast into foil 1.6 cm in diameter and 2 mm thick. The electrode foil was assembled in a cylindrical holder (exposed area 1 cm^2). After acetone cleansing the electrode was placed in the electrochemical setup. A stainless steel plate was used as the cathode which was placed at the other end of the setup. The aqueous electrolyte was prepared from lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$; AR 90.0%), sodium hydroxide (NaOH; AR 99.5%), and de-ionized water. The volume of the cell electrolyte was 2000 mL of solution for each test. The solution was prepared to yield concentrations of 4 M (mol L^{-1}). In literature [6] the researcher used organic additives to reduce the parasitic direct corrosion reaction between lithium metal and the electrolyte. In order to obtain a better hydrogen inhibition effect, four additives were selected as hydrogen inhibitors as recommended by other authors [6]: ethanol (AR 99.7%), triethanolamine (AR 90.0%), triethylene glycol (AR 90.0%), lead nitrate ($Pb(NO_3)_2$ AR 90.0%) [18]. The former three additives reduce the activity of the water by forming intermolecular hydrogen bonding between the organic additive and water. In the latter additive Pb enhanced hydrogen evolution over-potential at the lithium anode. The electrolyte was circulated through the pump and the fresh electrolyte was introduced from the bulk to the electrode surface. The solution flow rate was fixed at 18 L h^{-1} using a rotameter with scales and floats. An inverted funnel burette was placed above the anode in order to collect the evolved hydrogen. The current in the circuit was recorded by an amperometer. The whole electro-bath was placed in a constant temperature water bath box. The analyses of phase compositions and micro-structural morphologies were conducted by using X-ray diffraction (XRD) and scanning electron microscope (SEM, JSM-6360). For each sample, the measurements were performed at least twice and the average values of data points were obtained. The cathodic and anodic partial current densities were computed as $-2FN_{H_2}$ and $I_T + 2FN_{H_2}$. The current efficiency of the system (η) was calculated using the following equation:

$$\eta = \frac{I_T}{I_T + 2FN_{H_2}}[19,\ 20] \tag{1}$$

where I_T represents the total current density, F and N_{H_2} are Faraday's constant (F = 96485C/equiv) and hydrogen evolution rate, respectively.

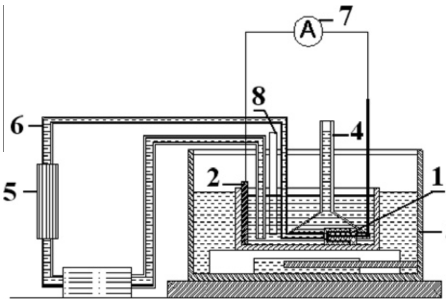

Fig. 2. Schematic electrochemical setup used for electrochemical measurement of the anode [13] 1. Lithium anode; 2. Stainless steel blade; 3. Constant temperature water tank; 4. Burette; 5. Flowmeter; 6. Electrolyte circulation system; 7. Amperometer; 8. Thermometer.

3. Results

3.1. The hydrogen evolution and discharge of lithium and lithium–cerium alloy

Fig. 3 shows the current density curves for lithium and lithium–cerium alloy in 4 M alkaline electrolyte at 25 °C. The evolved hydrogen rates and hydrogen volume in 20 min at the lithium and lithium–cerium alloy anodes in aqueous alkaline electrolyte are presented in Figs. 4 and 5, respectively. These data were obtained in static solution, that is, the solution was not circulated. As can be seen in Fig. 3, the lithium–cerium alloy current density was lower than that of the pure lithium anode, while the hydrogen evolution rate and hydrogen volume at the lithium–cerium electrode were slightly lower than that of lithium with the aid of the linear fit, as shown in Figs. 4 and 5.

The lithium–cerium anode containing 0.08 wt.% cerium showed a better hydrogen inhibition effect than lithium and its discharge current density was between 60 mA cm^{-2} and 70 mA cm^{-2}. The current density followed in the order Li > Li–0.08 wt.% Ce, while the hydrogen evolution rate and hydrogen volume at the anode followed in the order Li > Li–0.08 wt.% Ce.

The current efficiencies of lithium and lithium–cerium alloy are shown in Fig. 6. The curves in Fig. 6 were generated from the data in Figs. 3 and 4 using Eq. (1). It can be seen that the current effi-

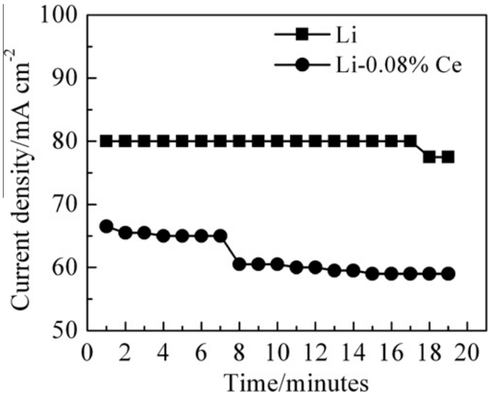

Fig. 3. Current density of lithium and lithium–cerium alloy anodes at 25 °C.