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Effect of temperature on the discharge and hydrogen evolution of lithium in alkaline aqueous solution

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ABSTRACT

The effects of temperature on the discharge and hydrogen evolution of lithium anode in 4 M (mol L^{-1}) LiOH solutions were investigated via hydrogen collection, polarization and SEM (scanning electron microscope). It was found that the hydrogen evolution rate is low below 30 °C with low discharge current density and the discharge current density is high over 30 with high hydrogen evolution rate. The lithium anode shows the better electrochemical performance with high discharge current density, low hydrogen evolution, and less porous film at 30 °C at 0.94 m s^{-1} in 4 M LiOH solutions.

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1. Introduction

Lithium is a highly reactive metal with quite negative standard potential and high dissolution rate in alkaline aqueous solutions [1]. It is feasible to develop high power, high specific energy lithium–water batteries with these characteristics stated above [2]. However, the direct parasitic corrosion reaction of lithium with water results in efficiency losses of lithium anode and safety problem due to the hydrogen evolution on the surface. Corrosion reaction leads to heat generation. It is very important to investigate the electrochemical behavior lithium in alkaline aqueous solutions at different temperatures. The effect of electrolyte temperature on the discharge, hydrogen evolution behavior, and surface morphology of lithium anode in lithium hydroxide solution was investigated in this paper using hydrogen evolution rate at OCP, potentiodynamic polarization, potentiostatic polarization, and scanning electron microscope.

2. Experimental

The experiments were performed in a conventional three-electrode cell assembly. The electrochemical cell included lithium (purity no less than 99.95%, 2 mm in thicknesses, and 16 mm in diameter) as the working electrode, a Hg/HgO reference electrode, and a platinum foil counter electrode. The working electrode was assembled in a cylindrical holder (exposed area 1 cm^2) and was degreased in acetone before each test. An inverted funnel buret was placed above the working electrode to collect the volume of hydrogen gas evolved during the reaction. The aqueous electrolyte was prepared from lithium hydroxide monohydrate ($LiOH\cdot H_2O$; AR 90%) and deionized water. The concentration of the solution was 4 M (mol L^{-1}). Electrochemical tests were measured with a CHI660C electrochemical measurement system made by CH Instruments, Inc. Shanghai, China. The potentiodynamic polarization was carried out from a cathodic potential of −3.2 V to an anodic potential of 0 V with respect to the reference electrode (Hg/HgO) potential at a sweep rate of 0.01 V s^{-1}. The data has been processed for evaluation of the open circuit potential kinetic parameters by plotting E versus $\log i$ curves. The potentiostatic polarization was determined with the potential being maintained constant for 400 s to obtain the stable current and the hydrogen rate. The potential was then stepped to the next value and the procedure was repeated. The cathodic and anodic partial current densities were computed as $-2FN_{H_2}$ and $I_T + 2FN_{H_2}$, respectively. The coulombic efficiency of the system (η) was calculated from the following equation,

$$\eta = \frac{I_T}{I_T + 2FN_{H_2}} \tag{1}$$

where I_T represents the total current density, F and N_{H_2} are Faraday's constant (F = 96,485 C/equiv) and hydrogen evolution rate, respectively [3,4].

For each sample, the measurements were carried out at least three times and the average values of data points were obtained.

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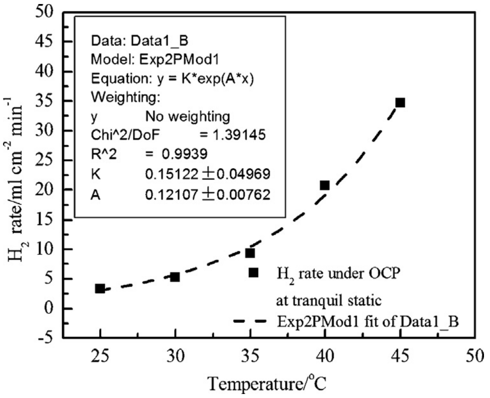

Fig. 1. Hydrogen evolution rate of lithium anode under OCP in 4 M LiOH at various temperatures at tranquil static. The curve is generated by software.

3. Results and discussion

Hydrogen evolution rate of lithium in 4 mol L^{-1} LiOH at various temperatures at tranquil static under open circuit potential (OCP, −2.7VSHE) is shown in Fig. 1. It can be seen from Fig. 1 that the hydrogen evolution rate of lithium increases with increasing solution temperature under OCP. The experimental data can be fitted well using exponential growth. This suggests that increasing temperature accelerates the corrosion rate of lithium in alkaline aqueous solution. The corrosion rate increases slowly between 25 °C and 30 °C and it increases drastically after 35 °C. The experimental point can be fitted very well using exponential increase. Under OCP, lithium reacts with water as the followings

$$2Li + 2H_2O = 2LiOH + H_2 \tag{2}$$

Lithium hydroxide is generated at the lithium/water interface continually. At ambient temperature (25 °C), the solubility of LiOH is low. The solubility of LiOH in water at 298 K has been reported to be 5.234 mol/kg (12.9 g LiOH per 100 g water) [5,6]. In this case, the recrystallization rate of LiOH is bigger than solution rate. As a result, the lithium surface film becomes thick and less porous. It is not easy for water to penetrate into the active site of the inner layer. So the hydrogen evolution rate is small. The solubility of LiOH increases with increasing the temperature. The lithium surface film becomes thin and more porous due to the bigger solution rate of LiOH than recrystallization rate. It is easy for water to penetrate into the active site of the inner layer. So the hydrogen evolution rate increases with increasing the temperature.

The potentiodynamic polarization of lithium in 4 mol L^{-1} LiOH at different temperature is shown in Fig. 2. It can be seen from Fig. 2 that the open circuit potential marginally shifts in the positive direction with increasing the temperature. Both the anodic polarization current density and the cathodic polarization current density increase with increasing the temperature. It shows that both the anodic process and the cathodic process are promoted with temperature increasing. A good discharge performance is difficult to be available when the temperature is below 25 °C because the anodic process is inhibited. When the temperature is 35 °C, the anodic polarization is smaller than that at 25 °C or 30 °C but its cathodic hydrogen evolution reaction increases. From the polarization results, we concluded that lithium anode shows a better discharge performance at 30 °C than that at 25 °C or 35 °C.

Table 1
Corrosion parameters obtained from potentiodynamic polarizatioin studies on lithium anode in 4 M LiOH at various temperatures at tranquil static.

Temperature (°C)	E_{corr} (V)	i_{corr} (A cm^{-2})	R_p (Ω cm^2)
25	−2.873	0.04557	1.3
30	−2.867	0.04713	1.2
35	−2.865	0.06262	0.9

The corrosion parameters such as open circuit potential (E_{corr}), corrosion current density (I_{corr}), which is the total anodic dissolution current at the OCP, and polarization resistance R_p derived from Fig. 2 are given in Table 1. All these parameters above are automatically created from CHI660C software by fitting the polarization curves from 60 mV to 120 mV with respect to the open circuit potential.

Table 1 exhibit that the corrosion current density increases with increasing the temperature. The corrosion current density increases drastically when the temperature reaches 35 °C. The polarization resistance values decrease from 1.3 Ω cm^2 to 0.9 Ω cm^2. Increasing the solution temperature marginally shifts the open circuit potential in the positive direction. Therefore, the corrosion rate of lithium anode increases based on the corrosion current density and polarization resistance results [7,8].

Lithium–water battery functions well in the circulated electrolyte [2]. Therefore, it is necessary to investigate lithium performance at different temperature in the fixed rate of electrolyte. Polarization curves of lithium in 4 mol L^{-1} LiOH at different temperature at 0.94 m s^{-1} are shown in Fig. 3. It can be seen from Fig. 3 that there is no evident passivation section on the anodic polarization curves compared with that at tranquil static (Fig. 2). The anodic polarization current density is clearly higher than that when the solution is not circulated (Fig. 2). It indicated that solution circulation contributes to film dissolution and high discharge current density. The figure shows that both the anodic polarization current density and the cathodic polarization current density

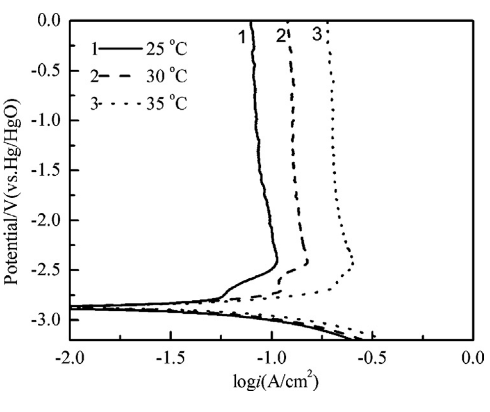

Fig. 2. Polarization curves of lithium in 4 M LiOH at various temperatures at tranquil static.

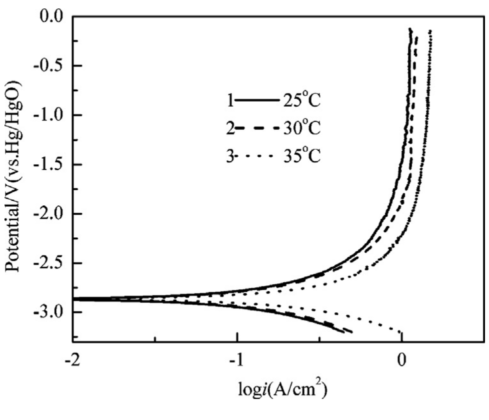

Fig. 3. Polarization curves of lithium in 4 M LiOH at various temperatures at 0.94 m s^{-1}.

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