Journal of Power Sources 299 (2015) 66–69

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

The effect of crystal orientation on the aluminum anodes of the aluminum–air batteries in alkaline electrolytes

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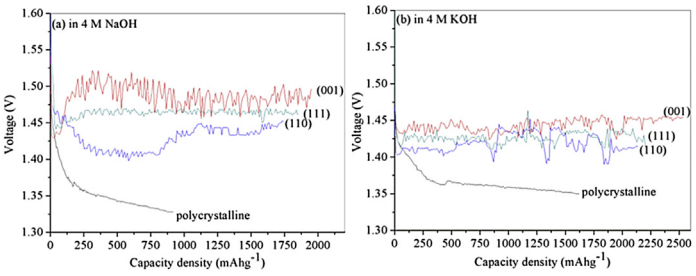
HIGHLIGHTS

- The electrochemical performance of Al is anisotropic.
- The capacity density of (001) plane is better than (110).
- The performance of polycrystalline Al as the anode is worse than single crystals.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 May 2015
Received in revised form
14 August 2015
Accepted 26 August 2015
Available online xxx

Keywords:
Crystal orientation
Aluminum anode
Al–air battery
Alkaline electrolytes

ABSTRACT

Recently, aluminum–air (Al–air) batteries have received attention from researchers as an exciting option for safe and efficient batteries. The electrochemical performance of Aluminum anode remains an active area of investigation. In this paper, the electrochemical properties of polycrystalline Al, Al (001), (110) and (111) single crystals are investigated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) in 4 M NaOH and KOH. Hydrogen corrosion rates of the Al anodes are determined by hydrogen collection. Battery performance using the anodes is tested by constant current discharge at 10 mA cm^{-2}. This is the first report showing that the electrochemical properties of Al are closely related to the crystallographic orientation in alkaline electrolytes. The (001) crystallographic plane has good corrosion resistance but (110) is more sensitive. Al (001) single crystals display higher anode efficiency and capacity density. Controlling the crystallographic orientation of the Al anode is another way to improve the performance of Al–air batteries in alkaline electrolytes.

1. Introduction

Increasing concerns about climate change and fossil energy supply limitations have made the need for green energy that produces less CO_2 more critical. The development of fuel cells that can convert the chemical energy from a fuel into electricity through a electrochemical reaction is an exciting area of current research. Metal fuel cells as an integral part of the new energy have become the hot spot for scientists [1]. Aluminum is one of most popular anode materials for these fuel cells. Aluminum has many desirable properties, including high energy density (8.1kWhkg^{-1}), environmentally friendliness, recyclability, abundance and economical [2–6]. However, practical applications of the Al–air battery have been stymied by its low coulomb efficiency caused by the high corrosion rate in alkaline electrolytes. To solve this problem, researchers have investigated multiple elements such as Mg, Ga, In, Sn, etc [7–11] and corrosion inhibitors [12–15] in the past decade.

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http://dx.doi.org/10.1016/j.jpowsour.2015.08.095
0378-7753/

Previous studies have shown that change grain size can affect corrosion resistance [16–20]. Some reports have suggested the crystallographic orientation of the materials may be related to the electrochemical performance, including Pt [21], Au [22], Zn [23], Mg [24], and $LiCoO_2$ in a lithium ion battery [25]. There are few reports on the electrochemical properties of Al anodes with different crystallographic orientations. Aluminum with has a face-centered cubic structure is anisotropic from the point of view of material science.

This paper reports the electrochemical performance of Al anodes with different crystallographic orientations and the impact on the performance of Al–air batteries. The effect of crystallographic orientation on Al anodes for Al–air batteries should be investigated further and incorporated into the design of future battery systems.

2. Experimental

2.1. Materials

The experiments were conducted using three different orientated single crystals of pure aluminum (99.99%) in 1 × 1 cm pieces, grown using the vertical Bridgeman method, and produced by KJ Group, USA. The crystallographic orientations tested here are (001), (110) and (111). For comparison, the same composition of polycrystalline Al as a control test sample was melted and cast in a cast iron mold under argon atmosphere. Disk-shaped samples were cut perpendicular to the height direction and the grain size of the cast polycrystalline Al is about 1.4 mm. Impurity content of the samples was shown in Table 1. The analysis method of metal element is inductive coupled plasma emission spectrometer (ICP) and the non-metals element is LECO. To be sure that their chemical compositions are identical, differently orientated single crystals are cut from the same single crystal ingot. The raw materials of cast polycrystalline and single crystal ingot came from the same ingot. The samples were encapsulated in epoxy, ground with emery paper and polished to no visible scratches, then cleaned with doubly distilled water. Finally, they were dehydrated using alcohol and dried with a hair dryer.

2.2. Measurements

XRD patterns of the samples were collected to detect the crystallographic orientation using a Rigaku D/Max2200 diffractometer (Cu Kα, λ = 1.5406 Å) at a scanning rate of 6° min^{-1}. Crystallography orientations of the four samples were confirmed by XRD, as shown in Fig. 1. The samples were encapsulated in epoxy with only 1 cm^2 exposed. Self-corrosion tests of the samples were performed in electrolytes for 1 h using hydrogen collection method to estimate the erosion rate of the Al anodes.

The electrochemical measurements were conducted using a standard three-electrode system employing a GAMRY reference 3000 electrochemical workstation, Pt sheet 20 × 20 mm in size as the counter electrode, mercury/mercuric oxide (Hg/HgO) as the reference electrode. Tafel polarization curves were measured from −0.5–1.5 V vs. OCP at a rate of 1 mV^{-1} after the open circuit potential (OCP) was measured more than 1 h to ensure the stability of the system. EIS measurements were carried out at open circuit potential with a 5 mV sine wave perturbation. The measuring frequency range was 100 kHz-0.1 Hz.

Table 1
Impurity content of samples.

Element	Max ppm	Element	Max ppm	Element	Max ppm	Element	Max ppm
As	3	Co	2	Cr	3	Fe	25
Ga	5	Ge	3	In	5	Mo	2
Ni	1	O	25	P	5	Pt	3
S	20	Sb	1	Se	1	Si	25
Sn	2	Te	2	Tl	1		

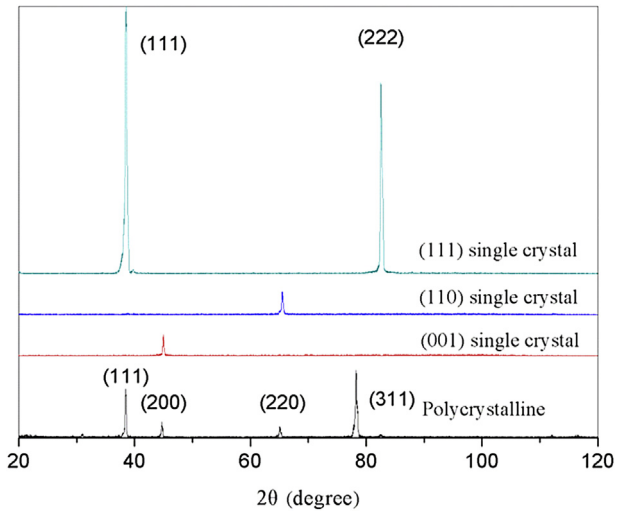

Fig. 1. XRD patterns of the samples.

The batteries consisted of anodes, cathodes and electrolytes. A commercial gas diffusion electrode including a gas diffusion layer and a catalytic active layer was prepared by laminating these materials together with a nickel mesh as a current collector. Each area of anode and cathode electrodes exposed to the electrolyte was 1 cm^2 under air condition. The test samples were used as the anodes. Al–air batteries were tested by constant current discharge at 10 mA cm^{-2} current densities for 3 h using the LAND test system.

The electrolytes were 4 M NaOH and KOH, experimental environmental temperature was 20 ± 2 °C.

3. Results and discussion

3.1. Self-corrosion and Tafel polarization curves

The low anode efficiency of Al electrode comes from hydrogen evolution reaction in alkaline electrolytes. The hydrogen evolution and Tafel polarization curves of the Al anodes in 4 M NaOH and KOH are shown in Fig. 2. The rate of hydrogen evolution increases in the following order in alkaline electrolytes: (001) single crystal < (111) single crystal< (110) single crystal < polycrystalline. The datas of Tafel polarization curves were processed using Gamry Echem Analyst software. Table 2 presents the corresponding corrosion parameters of the samples. The corrosion potential (E_{corr}) of (001) single crystal is the most negative. The E_{corr} increased in the following order in alkaline electrolytes: (001) single crystal < (111) single crystal< (110) single crystal. The corrosion current density (I_{corr}) shows a trend similar to the rate of hydrogen evolution. Trends were the same in both 4 M NaOH and KOH solutions. (110) surface was the easiest to corrode in the single crystals. For Al, the (001) plane has the lowest atomic density. A loosely packed plane has a lower binding energy due to the lower atomic coordination, so the atom has higher electrochemical activity. The polycrystalline Al has more grains with different orientations and crystal defects,