Performance of Al-0.1In-0.1Ga-0.1Sn-3.0Pb as anode for Al-air battery in KOH solutions

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Abstract. In this research, metal-air battery based on Al, Al-0.1In-0.1Ga, Al-0.1In-0.1Ga-0.1Sn, Al-0.1In-0.1Ga-3.0Pb, Al-0.1In-0.1Ga-0.1Sn-3.0Pb (wt%) is prepared and the battery performance is investigated by constant current discharge test in 4mol /L KOH solutions. The characteristics of the anodes after discharge are investigated by scanning electron microscopy (SEM) and self-corrosion rate measurement. The results show that Al-0.1In-0.1Ga-0.1Sn-3.0Pb has higher electrochemical performance and lower self-corrosion rate. Using Al-0.1In-0.1Ga-0.1Sn-3.0Pb as anode could improve the performance of Al-air battery, and solve the problem of severe self-corrosion and passivation.

1. Introduction

With the significant development of new energy vehicles, the metal air battery attract many attentions for its potential power source application[1-6]. Among them, the Al-air battery is quite promising due to its high energetic capacity (2980 Ah·kg⁻¹), the negative value of standard electrode potential (-1.66 V vs. Normal Hydrogen Electrode), low cost, and no pollution[7,8]. However, some disadvantages such as the self-corrosion of Al anode during battery discharge severely delayed its development and commercial exploitation. Also, owning to presence of oxide film, the active dissolution of Al is considerably slowed down and the corrosion potential of Al anode is shifted in the positive direction (about -0.8V vs. NHE) [9-13]. One effective way to enhance the Al anode performance is to alloy Al with other elements such as In, Ga, Sn, Pb, Hg, Mg, Zn etc. Alloying with In, Ga and Sn can shift the potential towards more negative, causing the so-called activation of Al[14]. Alloying with the elements of high hydrogen overpotential such as Pb, Zn and Sn can reduce the self-corrosion of Al anode and thus increase the anodic efficiency[14]. In this paper, the microstructure and electrochemical behavior of Al-0.1In-0.1Ga-0.1Sn-3.0Pb alloy as anode while using the alkaline solution as electrolyte of Al-air battery was investigated.

2. Experimental

2.1. Material preparation

Raw materials are commercial pure aluminum ingots, indium particle, gallium particle, tin particle, lead particle(>99.9%) for casting the experiment alloys. Raw material ingots were cut, dried, weighed the required amount of materials and melted in a corundum crucible in furnace under argon atmosphere at 720-760℃. The molten alloy was poured in a preheated cast iron dye. Then the Φ20mm×100mm ingots were got after natural cooling.

2.2. Electrochemical measurements

The electrochemical tests were carried out with three electrodes system at room temperature (25℃) by CHI1140 electrochemical test system (CHI Company, USA). A saturated calomel electrode (SCE) served as the reference electrode and a Pt sheet was used as the counter electrode. The working electrodes of open circuit potential (OCP) measured with an exposed area of 1 cm^2.

2.3. Self-corrosion

The samples of self-corrosion tests were cut to 20mm×20mm×5 mm, then ground with emery paper (grade 2000) and immersed in 4 mol/LKOH solutions for 30min. The released hydrogen was collected and recorded every five minutes. Then the corrosion products were rinsed by distilled water and ethanol.

3. Results and discussion

Table 1 presents the compositions of the alloys numbered as 1#, 2#, 3#, 4# and 5#. The nominal composition of 2# alloy is Al-0.1In-0.1Ga (wt%) which is shortened as Al-In-Ga. The nominal composition of 3# alloy is Al-0.1In-0.1Ga-0.1Sn (wt%) which is shortened as Al-In-Ga-Sn. And the 4# alloy is shortened as Al-In-Ga-Sn while the 5# alloy is shortened as Al-In-Ga-Sn-Pb.

Table 1. The compositions of the experimental alloys

samples	In	Ga	Sn	Pb	Al
1#	--	--	--	--	100
2#	0.1	0.1	--	--	remain
3#	0.1	0.1	0.1	--	remain
4#	0.1	0.1	--	3.0	remain
5#	0.1	0.1	0.1	3.0	remain

The open circuit potential and the anode utilization of the above aluminum alloy anodes were measured at room temperature using 4mol/L KOH solution as the electrolyte. As can be seen from Table 2, the corrosion potential of sample 1 is -0.88V,which is much more positive than its theoretical value due to the existence of oxide film on the surface. The corrosion potential of Al-In-Ga (-1.38V) is more negative than that of Al (-0.88V), which means that Al-In-Ga has higher electrochemical activity. The electrochemical activity increases in the following order: Al < Al-In-Ga-Pb < Al-In-Ga-Sn < Al-In-Ga-Sn-Pb< Al-In-Ga. It could be inferred that elements such as In and Ga could reduce the resistance of aluminum oxide film and thus cause the so-called activation of Al. By adding Sn and Pb, the anode utilization was improved since the elements can suppress the hydrogen evolution of aluminum alloy anodes. The anode utilization of Al-In-Ga-Sn-Pb is 93.5% while the current density is set 70mA • cm^{-2}. However, the corrosion potential slightly shifted positively compared to Al-In-Ga.

Table 2. The corrosion potential and anode utilization of five aluminum alloy anodes

Samples		1#	2#	3#	4#	5#
corrosion potential (V vs. SCE)		-0.88	-1.38	-1.29	-1.24	-1.36
anode utilization (%)	25(mA·cm^{-2})	42.9	57.9	55.7	44.6	73.0
	50(mA·cm^{-2})	67.4	73.3	83.1	76.3	87.9
	70(mA·cm^{-2})	75.7	86.4	87.3	82.1	93.5

Fig.1 shows the discharge potentials of five alloys at different current densities. It can be seen obviously that the potential of Al is most positive, indicating that the addition of alloying elements can active the aluminum anode. The potential of Al-In-Ga alloy was most negative at low current density. But with the increase of current density, it decreased rapidly and became most positive when the current density reached 80 mA·cm^{-2}. The potential change rate of Al-In-Ga-Sn-Pb anode is the most

gentle, indicating that the common addition of Sn and Pb elements can improve the working potential, which is consistent with the anode utilization test results.
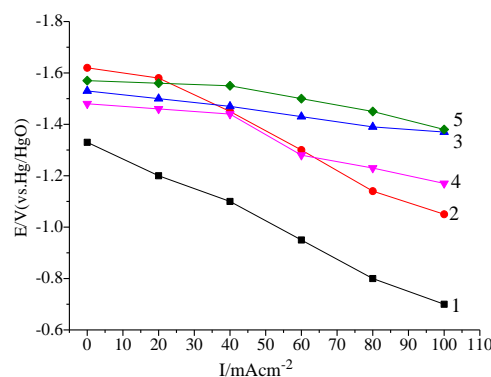

Fig.1 Working potential curves of 5 samples at different current densities in 4 mol / L KOH solution (25°C)

The self-corrosion behavior of five alloys in 4mol/L KOH solution was studied. The hydrogen evolution curves were shown in Fig.2. The most severe self-corrosion occurred in Al-In-Ga-Sn alloy and the hydrogen evolution rate is five times more than that of pure Al. Then is the Al-In-Ga alloy, which is 1.5 times of pure Al. The self-corrosion of Al-In-Ga-Pb and Al-In-Ga-Sn-Pb is close to pure Al. The results indicated that the addition of In, Ga, Sn can activate the anode while Pb in the Al alloy could play a role in inhibiting its self-corrosion. The reason may be that the In, Ga, Sn, especially Sn, could destroy the oxide film on the aluminum surface. The Sn^{4+} replaces the Al^{3+} in the oxide film, producing an additional hole and destroys the density of the oxide film. And Sn may be segregated from the co-melt alloy in the form of particles, and then the metal particles fall off. Thus the contact area of aluminum and KOH solution increased, exacerbating the hydrogen evolution. With the reaction of the alloy and KOH solution, a layer of black film was generated on the surface, which hindered contact surface between the anode and the solution. In this way, the hydrogen evolution was effectively inhibited. And that explained the hydrogen evolution rate tends to decrease in 20 to 30mins. The reason that Pb can inhibit its self-corrosion in Al alloy may due to its high hydrogen evolution potential.
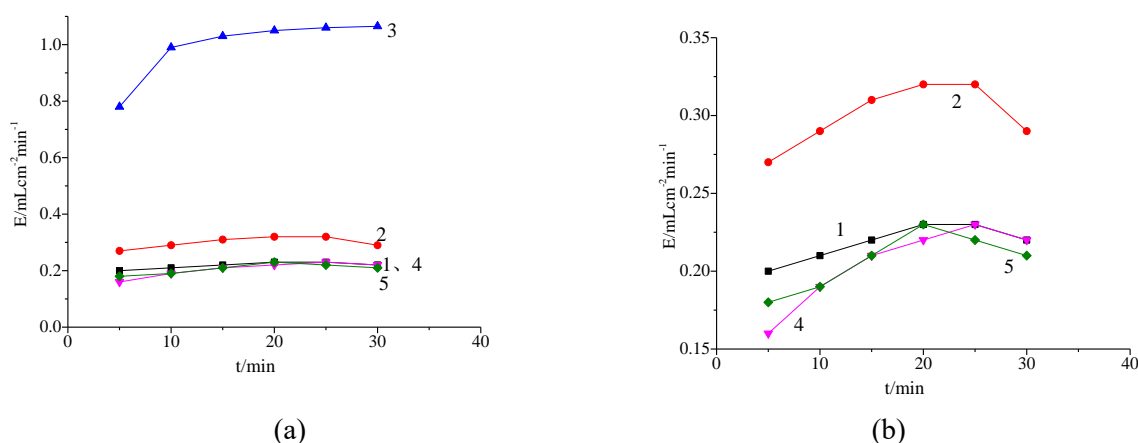

(a)   (b)

Fig.2 The hydrogen evolution curves of five anode alloys in 4mol/L KOH solution (25 ℃)

The surface morphologies of different anodes after discharge for 30min in 4mol/L KOH solution were obtained by scanning electron microscopy examination. As shown in Fig.3, the morphology of

Al shows few small pits in Fig. 3(a). As can be observed in Fig.3(b)and 3(c), the morphologies of Al-In-Ga and Al-In-Ga-Sn anodes after discharge, are loose with many pores and cracks compare with Fig. 3(a)and (e). The relative passivity morphology of Al results from the surface hydroxide layer. Pure aluminum, is unsuitable for use as the anode of an Al-air battery since its surface is covered by a passive hydroxide layer creating high overpotential during anodic dissolution. By alloying with particular elements such as In, Ga, and Sn, the aluminum anode was activated because the passive layer was broken down. On one hand, the low melting point alloying elements Sn and Ga distribute evenly on the solid solution of Al or in the grain boundary, destroy the Al lattice, and it can't generate continuous passive film on the surface; On the other hand, the alloying elements with low melting point and high hydrogen evolution overpotential dissolve and deposition on the aluminum surface again, which always make the alloy in the highly active state. The addition of Pb to aluminum as an alloying element has been shown to reduce the corrosion rate of aluminum.
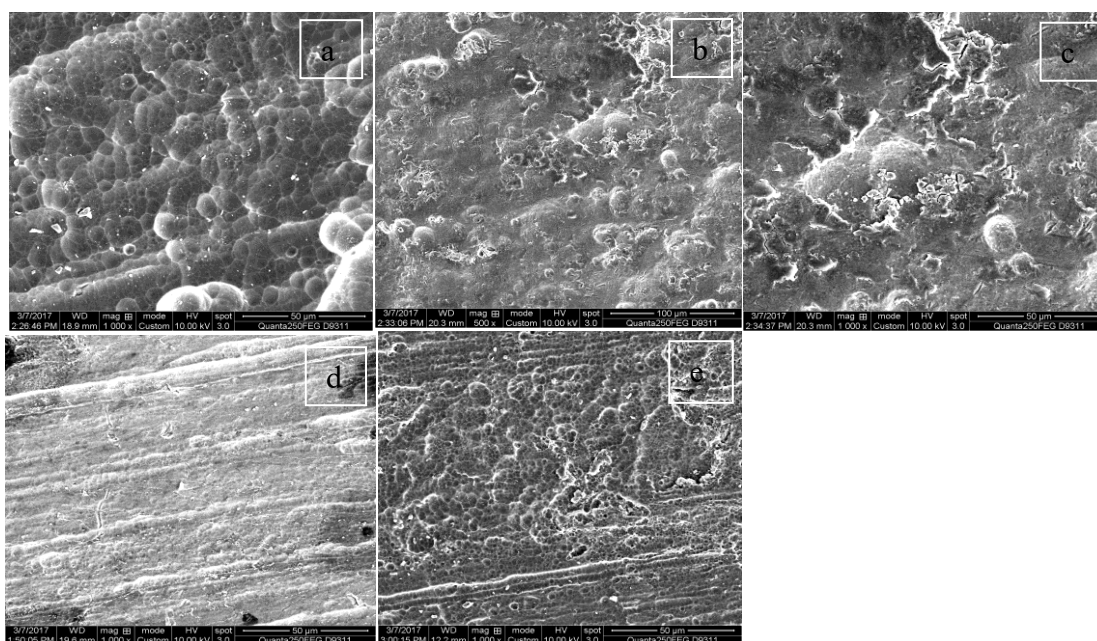

Fig.3 SEM images of different anodes after discharge for 30min in 4mol /L KOH solution
(a)Al, (b) Al-In-Ga,(c) Al-In-Ga-Sn,(d) Al-In-Ga-Pb,(e) Al-In-Ga-Sn-Pb,

4. Conclusions

We investigated the corrosion behavior and discharge performance of Al, Al-In-Ga, Al-In-Ga-Sn, Al-In-Ga-Pb, and Al-In-Ga-Sn-Pb anodes in 4mol · L^{-1} KOH solutions. Compared with Al and Al-In-Ga, Al-In-Ga-Sn-Pb has higher electrochemical performance and lower self-corrosion rate. SEM results of the alloy are in good agreement with corrosion characteristics. It has been observed that the Al-air battery based on Al-In-Ga-Sn-Pb offers higher operating voltage and anodic utilization than those with others. The corrosion potential of Al-In-Ga-Sn-Pb is -1.36 V. At a current density of 70mA cm^{-2}, the anodic utilization is 93.5%.

References

[1]   Shaohua Yang, Harold Knickle. Design and analysis of aluminum/air battery system or electric vehicles[J], Journal of Power Sources, 2002,112: 162–173

[2]   Qingfeng Li, Niels J Bjerrum. Aluminum as anode for energy storage and conversion: a review[J], Journal of Power Sources, 2002, 110:1-10

[3]   Zhonghao Rao, Shuangfeng Wang. A review of power battery thermal energy management[J], Renewable and Sustainable Energy Reviews, 2011, 15:4554-4571

[4]   Alexander Kraytsberg, Yair Ein Eli. Review on Li air batteries Opportunities, limitations and perspective[J], Journal of Power Sources, 2011, 196:886-893

[5]   Pucheng Pei , Keliang Wang, Ze Ma. Technologies for extending zinc air battery's cycle life: A review[J], Applied Energy, 2014, 128:315-324.

[6]   Dennis Wittmaier, Simon Aisenbrey, Norbert Wagner, KAndreas Friedrich. Bifunctional, Carbon-Free Nickel/Cobalt-Oxide Cathodes for Lithium-Air Batteries with an Aqueous Alkaline Electrolyte[J],Electrochimica Acta, 2014, 149:355-363

[7]   Lei Wang, Wentao Wang, Guandong Yang , Dong Liu , Jin Xuan, Huizhi Wang, Michael K.H. Leung , Fude Liu. A hybrid aluminum/hydrogen/air cell system[J], International journal of hydrogen energy, 2013, 38:14801-14809

[8]   Xin Zhang, Shao Hua Yang, Harold Knickle. Novel operation and control of an electric vehicle aluminum/air battery system[J], Journal of Power Sources, 2004, 128:331-342

[9]   Maria Nestoridi, Derek Pletcher, Robert J K Wood, Shuncai Wang, Richard L Jones, Keith R Stokes, Ian Wilcock. The study of aluminium anodes for high power density Al/air batteries with brine electrolytes[J], Journal of Power Sources, 2008, 178:445-455

[10]   Ryohei Mori. A new structured aluminium–air secondary battery with a ceramic aluminium ion conductor[J], The Royal Society of Chemistry 2013, 3, 11547-11551

[11]   Ryohei Mori. A novel aluminum-air secondary battery with long-term stability[J], the Royal Society of Chemistry, 2014, 4：1982-1987

[12]   D R Egan, C Ponce de León, R J K Wood , R L Jones, K R Stokes, F C Walsh. Developments in electrode materials and electrolytes for aluminum air batteries[J], Journal of Power Sources, 2013, 236:293-310

[13]   D Gelman, B Shvartsev, Y Ein Eli. Aluminum air battery based on an ionic liquid electrolyte[J], Journal of Materials Chemistry A, 2014, 2(47):20237-20242

[14]   Performance of Al-0.5 Mg-0.02 Ga-0.1 Sn-0.5 Mn as anode for Al-air battery in NaCl solutions[J], Journal of Power Sources, 2014, 253: 419-423