The Research of Aluminum/Air Battery*

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Abstract: Aluminum is an abundant and cheap non-ferrous metal. As a new-fashioned fuel cell, the aluminum/air battery has been attaching importance, due to its low-cost, high power and energy density. This paper describes the mechanism of the Al/air battery, and summarized the research and advancement about air cathode, Al anode, catalysts, and electrolyte.

Key words: aluminum/air battery; Al anode; air cathode; catalyst

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Metal/air fuel cells include Al/air battery, Zn/air battery, Fe/air battery and so on. Among of them, Al/air battery which is mainly made of Al has many electrochemistry virtues, such as abundance, cheap cost, innocuity, high power density, high energy density and so on. Hence, it catches foreign researchers' eyes. The Al/air battery, or semi-fuel cell, has been demonstrated to be commercially viable in military and civil applications, including underwater propulsion systems, back-up power sources for telecommunications systems and portable power sources[1]. The development of the Al semi-fuel cell has resulted in a number of products ranging from emergency power supplies, to main or auxiliary power systems for electric vehicles, boats, submarines and other submersible vehicles. Oversea products using Al semi-fuel cell technologies that are now being marketed include low-cost air cathodes, components for marine propulsion batteries[2], reserve batteries for telecommunication systems[3] and Al-oxygen underwater propulsion systems. As a power system for underwater exploration, the Al semi-fuel has been demonstrated to provide power ten times more than the nickel-cadmium batteries it replaced and to substantially reduce the time taken to recharge a vehicle. The neutrally buoyant underwater propulsion system, equipped with a completely self-contained oxygen supply, has energy densities up to 500 $W \cdot h \cdot L^{-1}$ and delivers 2.3 kW at 60 V. With an endurance of 50 hours at 2 kW, the range of a typical underwater vehicle is extended from 50 to 300 km. A portable battery to power military communications equipment directly, or to recharge secondary nickel-cadmium batteries, weighs less than 4.5 kg, yet is capable of generating 300 watts of power. The system has a lower life cycle cost and generates comparable or better energy density than the lithium cells currently being used[4].

However, the Al/air battery still has some dissatisfactory places. In electrolyte, whether under the condition of open-circuit or during discharge, Al is easily corroded with hydrogen releasing. At the same time, the oxide film on the surface of the Al electrode restrains the electrochemical performance of Al. The research on Al/air fuel cell is mainly around the anode, cathode, catalyst, electrolyte, and the battery design and reaction mechanism in order to eliminate the restrains and utilize its advantages. This paper introduces mainly the progress on Al/air battery in the world.

1 Mechanism of Al/air battery

Al/air fuel cell generates electric power through "fuelling" aluminum. The cell consists of aluminum plates, an air cathode and an electrolyte. In this battery, aluminum, which is an abundant and cheap non-ferrous metal, is the fuel, while oxygen in the air is the combustion-supporting gas. A cell fueled by aluminum generates power through simple electrochemical reaction between the metal, which is placed in a saline or alkaline solution, and oxygen from the air. Electricity is produced as the aluminum oxidizes.

The Al anode (the negative electrode) is dissolved, liberating 3 moles of electrons/mole of Al, whereas oxygen is reduced at the cathode to hydroxyl ions under the consumption of electrons and water:

Cathode: $$3/4O_2 + 3/2H_2O + 3e^- \longrightarrow 3OH^- \quad (1)$$

Anode: $$Al + 4OH^- \longrightarrow Al(OH)^{4-} + 3e^- \quad (2)$$

$$Al(OH)^{4-} \longrightarrow OH^- + Al(OH)_3 \quad (3)$$

Sum: $$Al + 3/4O_2 + 3/2H_2O \longrightarrow Al(OH)_3 \quad (4)$$

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At the same time, a corrosion reaction between the anode and the electrolyte also occurs, generating hydrogen rather than useful electricity.

$$Al + 3H_2O \longrightarrow Al(OH)_3 + 3/2H_2 \qquad (5)$$

Electrification of the battery is mechanical. That is going on charging by replacing Al pole and electrolyte. To recharge the cell when the Al is consumed, the plates are replaced and more electrolytes are added. Therefore, it is called mechanically chargeable battery、

2 Research on Al anode

Aluminum has special electric structure. Al^{3+} has three covalent bonds and three copulate bonds. Aluminum is solvent in acid and alkaline solution, and has varied chemical forms. Moreover its resistance rate is just 2.76 $\mu\Omega \cdot cm^{-1}$, electrochemical molar quantity is 0.3356 $g \cdot A^{-1} \cdot h^{-1}$. Therefore, it is possible that aluminum is used in battery's research[5,6].

However, the Al/air battery still can't be entirely applied in commerce. Due to the highly corrodent speed in electrolyte, Al gives off a plenty of hydrogen, which leads to the sharp reduce of anodic Faraday efficiency. At the same time, oxidative film that covers the surface of Al decreases the anodic voltage efficiency. Hence, to improve its performances some microelements often are affiliated.

2.1 The elements lowing resistance of Al oxide

Many researches have proved that the elements, such as Ga, In, Sn and Bi, can decrease the resistance and increase the open circuit voltage[7,8]. In the early 1960s, Keir D S et al have found that Sn can obviously improve the electrochemical characters, move the Al potential to negative direction, and increase the current of Galvanic cell. The reason is that Sn^{4+} moves into the oxide film of Al, replaces Al^{3+} with cavity produced. This makes the resistance of the film decrease. However, Sn may separate out or deposit in the form of granule from the common fusion. It will increase autoecious erode. So it is more suitable to affiliate the other elements, such as Ga and In.

2.2 The elements making up of low melting point alloy

The aim of affiliating the elements making up of low melting point alloy is for meeting demands of the Al anode in the large current discharge. They compound the low melting point alloy that melts with Al completely in liquid, but is not soluble in solid. When the alloy solidified, they compound low melting point crystals or particles. The melting point is very low. They are melted down at the work temperature. The film will be changed into the structure of tiny bores. The real surface of the electrode is increased remarkably. Thereby the meeting surface between the electrolyte and the anode will grow. Therefore, during discharge, the film is easily collapsed. The discharge character is improved, and the potential will move to negative direction.

The United States Aluminum Industry Company has once studied low totally the melting point alloy constituted respectively with Ga, In, Sn, Zn, Bi, Cd, Pb, etc[7]. Among them, the melting point of the metal alloy GaInSnZn(61:25:13:1) is only 3 ℃. Then with 20% KCl as an electrolyte, and the saturated $HgCl_2/Hg$ electrode as the electrode for reference, the open circuit voltage of the electrode is -1.719 V, and the electric voltage is -1.261 V at 100 $mA \cdot s \cdot cm^{-2}$. The experiment has proved, inside pure Al the affiliation of element, which can become low totally the melting point of the metal alloy, can generally make the open circuit voltage move towards the negative direction above 500 mV. Regarding when current density as 100 $mA \cdot s \cdot cm^{-2}$, the pole potential can move to the negative direction 500 mV or so, and the function of its electrochemistry acquires the evident exaltation.

2.3 The elements of high released hydrogen overvoltage

The autoecious erode responds of aluminum usually accompanies with the evolved hydrogen reaction in the electrolyte. Therefore, we can repress the evolved hydrogen reaction through repressing the corrosion reaction of the Al. Because the development of evolved hydrogen reaction had relation with the electrode's hydrogen overvoltage, adding the elements of high hydrogen overvoltage can consumedly lower the autoecious erode, and increase its utilization. The Fe and Ni can lower the hydrogen overvoltage. But Pb and Hg will increase the hydrogen overvoltage. The metal elements of high hydrogen overvoltage still contain Cd, Sn, Tl, and Zn, etc. Their hydrogen overvoltages are from 1.2 to 1.5 V. It is noticeable that Hg is a deadly poison as well as Tl.

Abroad researches have already largely proceeded on formulation of Al metal alloys. Canada Aluminum Industry Company ELTECH has researched a few different composition Al metal alloys with high power density and high-energy output[8]. Among them, ratio energy of the metal alloy BDW ($AlMg_{0.1}In_{0.2}Mn$) attain 4.2 $kW \cdot h \cdot kg^{-1}$ when the current density is 200 $mA \cdot s \cdot cm^{-2}$ and power density is 0.6 $W \cdot h^{-1} \cdot cm^{-2}$. The United States Aluminum Industry Company's Mg-Ga-Al metal alloy and Sn-Ga-Al metal alloy, Renault Company's Rx808 metal alloy, and Canada Aluminum Industry Company BDW metal alloy all have already realized commercialization. The Al metal alloy used in the high power density battery that Southwest Aluminum Alloy Process research manufactured has already got the success. In this respect, they collected the beneficial experience. Al-Ga-Bi-Pb metal alloy anode made by Southwest Aluminum Processing Plant can attain goodly electrical functions. The average potential is -1.44 V, evolved content is lower, and is averagely $0.69\ mL \cdot h^{-1} \cdot cm^{-2}$, the reactant is easily shed off, and discharge is stable[8].

Moreover, the shape of the Al anode to functions of the battery also contains certain influence. The suitable shape of the anode can decrease the corrosion rate of the Al electrode, and enlarge the battery power and the current density. The Al anodes of cylinder[9], flat[10] and wedge[11], etc shaped electrodes, and the optimization of the electrode shape all have some researches.

3 Research on air cathode

Some main problems that exist in Al/air battery are attached to air cathode. The development of high efficient air cathode will make the battery power distinctly increase.

The core of Al/air battery is air cathode. It mainly includes carrier, catalyst and ventilate film. The diffused air electrode is constituted with several carbon layers interlaced by PTFE. They are not only a converting energy reaction area, but also providing a path for delivering air, and partition the electrolyte.

For the sake of the meeting different requests of physics and chemistry, usually the air electrode is a multilayer construction, and can be divided into two part: the first part provides the electrode's framework, and deci- des the electrode's machine strength degree; the second part insures air to deliver. Electrochemical reaction proceeds between these two parts, close to the boundary of three states crossed by the reactive air, electrolyte and an electric catalyst. The Activate layer is the basic as well as ventilated layer in the air electrode. They generally contain the catching current net, catalyst, and ventilated film etc. In the three-layer typical model (the catching current net, the well-ventilated layer and the activate layer), carrier is put one side of the air electrode for adapting to the double bore design. The air electrode that University of Wuhan manufactured has four layer constructions: the activate layer/waterproof and well-ventilated layer/the catching current and electric net/the watertightness well-ventilated electric layer[11]. Carrier is made of carbon with PTFE as the glue agent and metal oxides as the electric catalyst.

In the Al/air fuel cell's price the precious metal cata- lyst occupies a very heavy part. Precious metal catalyst is easily poisoned and very sensitive to sinter. Therefore, looking for the cheap efficient catalyst to replace the tradition precious metal catalyst will make the Al/air battery head for commercialization and practicality. In the beginning of 1990s, there is a bigger progress in the catalyst aspect, but in the last few years few further breakthrough. The big wreath activate carbon (such as the CoTMPP) can be used as that electric catalyst which is used for oxygen's reduce[12]. Especially its stability is increased with pyrogenation at high temperature, and this catalyst is also reserved good activity. Muknerjee et al[13] has researched the graphite metals, discovered that graphite, which metals handled, can be used as the changed cathode material of the Al/air battery. The metals include Pt, Ni, Cu, Fe, Co etc. The electrodeposited method is adopted in the proper electrolyte pond to manufacture the metal carbon. Experiments have proved that the discharge functions of the graphite air electrode wrapped by Pt, Ni or Cu show remarkable exaltation. Therefore, Pt, Ni and Cu have goodly catalysis. And the usage of Ni and Cu to wrap up the graphite can acquire the cheap efficient air electrode used for the Al/air battery. Muller et al[14] have prepared the big surface $La_{0.6}Ca_{0.4}CoO_3$ with primitive methods of the malic acid and the citric acid, and used it as the catalyst for the double functions air electrode. The efficacy was better. Although different metallic ions have different electric catalysis, it is remarkably that carbon used as carrier of catalyst also has certain catalysis.

4 Electrolyte in the Al/air battery

Otherwise the difference of electrolytes affect the battery performance. The electrolyte of the Al/air fuel cell can be a neutral salt aqua, and also can be an alkaline aqua. In salt aqua, the discharge product of the battery will become gelatinous. It enlarges resistance, and lowers the battery efficiency. But in alkali aqua, this kind of circumstance can't appear. Therefore from the view of the battery efficiency, the alkali aqua is better than the salt aqua. But the causticity of the alkali aqua is stronger, and the inconvenience is in the electrolyte's replacement. Therefore on the small power electric appliances the usage of the salt aqua (neutral electrolyte) is more practical and convenient. Regarding the seawater battery, the salt aqua also is viable. The neutral Al/air Battery of static electrolyte that Zhenya Li of the Tianjin University designed discharges at 2 A, the output of voltage to 10 V; then when the resistance is 10 Ω, the output of current to 0.136 A, the output of voltage is 1.36 V. When the weight of Al electrode is 4 g, the battery discharges at 10 Ω resistance about 8 h everyday, it can continue 6 days, and the decay rate of the electrode is small. The Al utilization is up to 55%[15].

Besides supporting the battery reaction, electrolyte still has another important function: dissolve the electrolytic product on the electrode and make the electrolytic product move out of the battery with the electrolyte, and repress corrosion of the anodic Al. If the electrolytic product adheres to the electrode, resistance inside the battery will be enlarged, and the battery efficiency will be lowered. Therefore a valid electrolyte system must be necessary to a good efficient battery system. Alkaline citrate and stannate together as the additive can repress Al from corrosion, and has no harmful influence to valid function of Al anode at high negative potential. The Al/air battery using that electrolyte can work under the normal temperature safely and availably. In the electrolyte containing citric acid and stannate, before $Al(OH)_3$ precipitated, the anti-corrosion of Al(99.99%) is very strong. The corrosive rate is only for 0.06 $mg \cdot cm^{-2} \cdot min^{-1}$. Through appended Na_2SnO_3 the anode's passivation also can be delayed, and the polari- zation of the Al electrode can be validly reduced[16]. Making use of peroxid as the electrolyte, Qistein Hasvold et al obtained the high-power practical Al/peroxid motive battery system[17].

5 The future and development of the Al/air battery

Overseas, the researches on Al/air fuel cell began from 70's, and have gained many fruits in recent 30 years. A lot of scientists give a high review on its preferences and prospect. After evaluating the Al/air battery of the Aluminum Energy Company, scientists of the Toronto University enounce: Although the Ni-MH battery and the lithium ion battery represent a time enormous advance at the battery technique, with the Al/air battery compared, their power become gloomy[18]. However, there are a few domestic researches on this aspect. It is overlooked in our country. It is believed that enlarging the research on the Al/air fuel cell, and studying the achievements of foreign countries, is what we now urgently demand.

Abroad various techniques about the Al/air batteries have been developed. Its commercial application has been proved. However, the most anodes are high-pure Al (pure degree is 99.99% above), and the price is very high. Actually the pure degree of industry Al is lower, because of existing of large quantity iron impurity. Its electrochemical function is far from that of high-pure Al. Therefore at the same time when the Al anode metal alloy researches, the study of industry Al anode's application should be proceeded. The continuous investigation of cheap efficient catalyst also pushes the Al/air battery forward. Moreover, reasonable efficient design of batteries demands further diligence. Only proceeding in-depth complete research on the Al/air battery, its business value can realize, and its advantage as a new power supply can appear. Our country is also a big country of aluminum industry, more enlarge researches on the Al/air battery theories and appliances, and lift the high-tech level, adequately use aluminum resources.

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铝-空气电池的研究

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摘　要：铝是一种丰富廉价的有色金属，铝-空气电池作为一种新型燃料电池，由于有低成本、无毒害、高功率、高能量密度等优点，受到了极大重视。阐述了铝-空气电池的工作原理，并对其阳极铝合金配方、空气阴极、催化剂、电解液等方面的研究概况进行了叙述，提出了铝-空气电池的研究发展方向。

关键词：铝-空气燃料电池；铝阳极；空气阴极；催化剂

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