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Study on titanium foil coated with partial reduction titanium dioxide as bipolar lead-acid battery's substrate

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HIGHLIGHTS

- A lay of TiO_{2-x} was coated on the Ti plate surface by sol–gel method.
- The properties of Ti foil's surface is the most excellent at 800 °C.
- Electrochemical performances of battery with Ti/TiO_{2-x} as substrate are superior.
- In the cell cycle, the properties of Ti/TiO_{2-x} as substrate can maintain stability.

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ABSTRACT

Pure titanium foil cannot be directly as the substrate for the bipolar lead-acid battery due to its surface oxidized into titanium dioxide in the cell cycle. The poor electronic conductivity of titanium dioxide will increase substrate's ohmic resistance and can affect the cell's electrochemical performances. In this paper, titanium foil's surface is coated with a lay of partial reduction titanium dioxide (TiO_{2-x}) which has excellent chemical stability and high electronic conductivity by means of sol–gel method. Through XRD, SEM and four-probe test, it shows that the modified titanium's surface has the most superior crystal structure and morphology and the highest electronic conductivity in the sintering temperature of 800 °C. We subsequently assemble bipolar lead-acid batteries with Ti coated by TiO_{2-x} as the substrate material. The batteries are discovered that when charged and discharged in 3.5 V–4.84 V at 0.5C the voltage between the charge and discharge voltage platform is 0.3 V, and the initial discharge specific capacity can reach 80 mAh g^{-1}. When the current rate is up to 1C and 2C, the initial discharge specific capacity is 70 mAh g^{-1} and 60 mAh g^{-1}. After 100 cycles, the initial specific capacity only decreases 12.5%.

1. Introduction

The increasing concern for environmental pollution problems and the lack of petroleum resources makes the whole world start to find a suitable method to deal with these problems. At present, people find that consuming petroleum resources and polluting environment are mainly originated from the development of the automobile industry. So it is expected that development of hybrid electric vehicles (HEV) or electric vehicles (EV) will provide an opportunity to improve the situation. In the operation of the HEV and EV, the battery is the essential element to determine its cost, using range and performance and so it has become the focus of the research. So far, various types of batteries can be as the power system for HEV and EV. It includes the lead-acid battery, Ni–MH battery, lithium ion battery, fuel cell and so on. Lead-acid battery is a type of the ideal power source for hybrid electric vehicles due to its simple structure, ripest craft, non-expensive technology, safety, and ease of recycling [1,2].Nevertheless, batteries for HEV need the higher specific power and specific energy and longer cycle life, however, traditional lead-acid battery can't meet these requirements. Therefore, we need find a kind of novel pattern lead-acid battery to replace it.

Bipolar lead-acid battery is a type of promising lead-acid battery system. It has turned into the lead-acid battery's internal structure. Inside the bipolar lead-acid battery, there are some bipolar plates which are the positive (lead dioxide) and negative (lead metal) active materials respectively placed on both sides of a metal substrate. The number of bipolar plates decides the battery's work

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voltage. And from the battery's structure, we can know that the more bipolar plates, the higher battery voltage. The schematic diagram of the bipolar lead-acid battery is presented in Fig 1.The electrochemical mechanism of bipolar lead-acid battery is similar to traditional lead-acid battery, thus it has all lead-acid battery's advantage. From Fig 1 we can see that in the charge and discharge process, the current vertically flows through the substrate from one cell to another. The current transfer mode can effectively shorten the current transmission path in order to reduce the ohmic resistance inside the battery and the current can be uniformly distributed on the surface of the substrate to decrease the active material's electrochemical impedance. Thus, the bipolar lead acid battery has the higher specific capacity and specific power and it can respond to the requirements of hybrid electric vehicles [3].

In the bipolar lead-acid battery, the substrate material is the most important part. It needs lightweight, corrosion resistance and high electronic conductivity. In the present reports, lead–tin alloy, ceramic, barium metaplumbate ($BaPbO_3$) and Ebonex® [4–6] were explored as substrate material for bipolar lead-acid battery. They were all ideal substrate material and some have previously started industrialization. Titanium foil is also an ideal substrate material due to its lightweight, high strength and corrosion resistance. From the bipolar plate structure, we can know that one side of the substrate for bipolar lead-acid battery is used as anode carrier and the other side as the cathode carrier. However, pure titanium foil as anode carrier is unreliable because its surface will be oxidized into a layer of titanium dioxide due to the positive high potential and strong oxidizing. This layer of titanium dioxide's low electronic conductivity will make the substrate of the bipolar lead no longer in force and the battery performance will be impacted seriously. Thus, the surface of titanium foils as substrate for bipolar lead-acid battery is expected to be modified.

Partial reduction titanium dioxide (TiO_{2-x}) is a kind of oxygen defective compound. There are limited oxygen vacancies in the titanium dioxide lattice. These oxygen vacancies can supply some channels for the electron conduction and so that, the electronic conductivity is more superior to titanium dioxide. In addition to the high electronic conductivity, this type of material also has outstanding chemical stability and binding with Ti foil very well. It can still keep stability in aggressive acid, alkali and oxidizing conditions [7]. At present, the synthesis method of TiO_{2-x} is just by means of reducing TiO_2 with hydrogen or carbon [8–10] at elevated temperature. Therefore, coating TiO_{2-x} on the Ti surface firstly needs to coat a lay of TiO_2 on its surface and then reduces it at the elevated temperature. Currently, major methods for coating TiO_2 on the Ti surface include chemical oxidation method [11], anodic oxidation method [12,13] and sol–gel method [14,15].

In this paper, we firstly coated a layer of TiO_2 with carbon source on the titanium foil surface using sol–gel method and then sintered it at the elevated temperature in high purity argon atmosphere. Influences of titanium surface at different sintering temperatures were characterized through XRD, SEM and four-probe test. Subsequently, electrochemical performances of positive active material of bipolar lead-acid battery with modified titanium foil as substrate were also described by means of the charge and discharge test.

2. Experimental

2.1. Pretreatment of titanium foil

Before modifying titanium foil, it needs to be pretreated in order to improve its combination. 0.2 mm thickness of titanium foils were selected as the matrix. Firstly, they were soaked in saturated $NaCO_3$ solution at 60–70 °C to remove the surface grease. Secondly, they were mechanically polished with different abrasive papers, and washed clearly in an ultrasonic bath containing cold distilled water. Thirdly, chemically etched by immersion in HF: HNO_3:H_2O_2:H_2O (1:2:3:12 in volume) mixed solutions to remove the surface oxide. Lastly, washed in distilled water and dried in air completely at room temperature.

2.2. Coated with TiO_{2-x}

Before sintering the titanium foil, the surface need to coat with a layer of TiO_2/C with sol–gel method. The method was similar to preparing Ti/TiO_2 electrode [14]. However, the difference is the fact that it requires adding some carbon source as the reducing agent. The precursor solution for Ti coated with TiO_2/C was established by the following way. 1.7 mL of tetrabutylorthotitanate and 0.2 mL of hydrochloric acid (37 wt%), which prevent the precipitation of oxides and stabilize the solutions, were dissolved in 6.8 mL of ethanol. After stirring for 30 min at room temperature, a mixed solution of 1.0507 g of citric acid and 6.8 mL of ethanol was tardily added to the above solution with a burette under stirring vigorously. After the mixture was agitated for 30 min, a clear sol was formed. Finally, 1 g of polyethylene glycol (PEG-2000) was in addition to the above solution to reduce its surface tension. And then, the solution was kept standing to perform hydrolysis reaction for 10 h that can lead to the formation of TiO_2 sol. In the process of hydrolysis reaction, the temperature should be between 25 °C and 35 °C. Too high temperature would destroy the stability of the TiO_2 sol, while too low temperature would make polyethylene glycol precipitated from the solution. Put the pretreated titanium foils into the TiO_2 sol solution for 30 s and then taken out in the air and dried the titanium foils at 80 °C for 1 h in order to remove organic components. After that the surface of the titanium foils was coated with TiO_2/C. At last the titanium foils were sintered at 600, 700, and 800 °C in high purity argon atmosphere for 2 h.

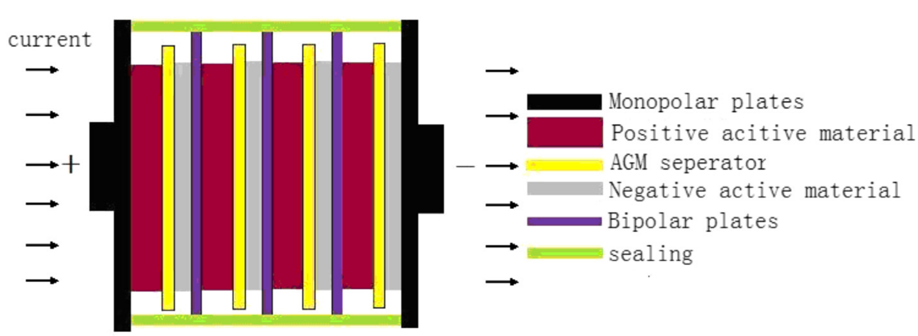

Fig. 1. The schematic diagram of the bipolar lead-acid battery.