Innovated a-C coating on PEMFC aluminum bipolar plates

Fuel cell is an efficient and environmentally friendly power generation system that directly and continuously converts chemical energy into electrical energy, which is the fourth type of power generation device after hydropower, thermal power and nuclear power. Among them, the proton exchange membrane fuel cell (PEMFC) has the advantages of high energy density, fast start-up speed at room temperature, and low operating temperature. As it can be treated as a mobile power source as well as a fixed power source, PEMFC was considered to be one of the ideal power sources to adapt to future energy and environmental requirements and has huge advantages in application in military, transportation, communications and other fields.

The bipolar plate is one of the core components of the PEMFC, which contributes a large part of the quality and cost of the battery pack. Bipolar plates are responsible for the functions of uniformly distributing the reaction gas, conducting current, and connecting the single cells in series. The ideal bipolar plate should have the characteristics of high thermal/electrical conductivity, corrosion resistance, low density, good mechanical properties, low cost and easy processing. Aluminum and aluminum alloys have lower density, higher specific strength, and better processing performance than titanium and stainless steel. The density of aluminum is only one third of that of stainless steel, and its conductivity is 21-44 times higher, besides the price is four times lower than that of titanium. The application of aluminum alloy bipolar plates can provide a higher specific energy density for the PEMFC stack, which is particularly important for the large-scale application of PEMFC in the transportation field. However, because the PEMFC operating environment usually contains aqueous solutions of F-, SO42-, SO32-, CO32-, HSO3- corrosive ions and the operating temperature is generally around 80℃, aluminum bipolar plates are prone to corrode or passivate in that working environment, the passivation layer increases the internal resistance of the battery, the dissolved metal ions may also lead to catalyst poisoning, causing the deterioration of battery performance.

In order to achieve high performance of PEMFC, both the corrosion and conductivity of the bipolar plate should be considered when the surface modification was applied on the aluminum plates. How to reduce the corrosion rate of the aluminum alloy bipolar plate and realize the reasonable matching of the conductivity and corrosion resistance of the bipolar plate is an urgent problem to be solved.

In this work, we propose a novel and effective strategy to deposit compact amorphous-C (referred as a-C) coatings by magnetron sputtering equipment on the 6061-aluminum alloy and the corrosion performance and conductivity of a-C coatings were balanced by annealing treatment. The coating system was equipped with four high purity graphite targets (99.99%) and the chamber was firstly vacuumed to get a background pressure below 5.0E-2 Pa. During the sputtering process, argon (99.9%) was introduced as the sputtering gas. Before the deposition, the plasma cleaning was carried out to get rid of aluminum oxides to get a more active surface. After that, the a-C coating layer was deposited immediately by introducing a negative substrate bias voltage of 100V, and the total deposition time was 4h. The a-C coatings whose thickness the were 250±5nm were then obtained. In order to balance the sp2/sp3 ratio of the coating, the vacuum annealing treatment was carried out by tubular annealing furnace GLS-1700X (Hefei kejing materials technology co., LTD).



Figure 1 Raman spectra of a-C coatings after annealing at different temperatures for 4h.

 The relative content of sp2 and sp3 of a-C coating was measured by Raman spectrometer (LabRAM HR Evolution, HORIBA Jobin Evolution, France) with an excitation wavelength of 532 nm after the annealing treatment at different temperatures, and the results were shown in Fig 1. It can be seen that the ID/IG ratio of a-C coatings was increased as the annealing treatment temperature increased, indicating that the sp3 was largely transferred into sp2 and the sp2/sp3 ratio was raised by the annealing treatment.



Figure 2 Contact resistance of a-C coatings after annealing at different temperatures for 4h.

The contact resistance of a-C coatings after different annealing parameters was measured according to the national standard GB/T 20042.6. The test area was 25cm2, an electronic universal testing machine (AGS-50kN, SHIMADZU) was applied to provide the pressure during the test, and the low resistance measuring instrument (RK2514, Shenzhen Meiruike Electronic Technology Co., Ltd.) was used to measure the resistance. The relationship between the contact resistance and the pressure of the coating after different annealing temperature was shown in Fig 2. It can be seen that the contact resistance was dramatically decreased after the annealing treatment. This can be attributed to the increased relative content of sp2 after the annealing treatment.



Figure 3 Corrosion behaviors of a-C coatings after annealing at different temperatures for 4h.

The corrosion behaviors of a-C coatings after annealing at different temperatures were measured by electrochemical work station (PARSTAT 4000A, Princeton Applied Research), and the results were showed in Fig3. It can be seen that the corrosion current density of aluminum substrate was 1.66×10-5 A⋅cm2 and was decreased to 3.72×10-6 A⋅cm2 after the a-C was deposited. The corrosion current density was greatly reduced to 8.51×10-7 A⋅cm2 after annealing at 500℃ and reached to the lowest corrosion current density of 6.31×10-8 A⋅cm2 after annealing at 550℃, however, the corrosion current density was increased after annealing at 600℃ to 4.57×10-7 A⋅cm2.

The corrosion performance of a-C is mainly attributed by the defects and the relative content of sp3, which was transferred to sp2 during the annealing treatment. The corrosion performance was increased after annealing at 500℃ and 550℃ because of the defects was repaired by the rearrangement of carbon atoms, and was decreased after annealing at 600℃ deduced to the reduction of sp3, the further research was needed for the detailed mechanism.