NOBLE METAL ALLOY CATALYST FOR LOW-TEMPERATURE FUEL CELLS AND PREPARATION METHOD THEREOF

Technical Field

This invention relates to the field of catalyst technology, specifically to a noble metal alloy catalyst for low-temperature fuel cells and a preparation method thereof.

Background Art

The durability of cryogenic proton exchange membrane fuel cells (PEMFCs) is one of the key challenges to their large-scale commercialization. Under dynamic operating conditions such as frequent vehicle start-stop and load changes, local fuel supply shortages can easily occur, leading to abnormally high electrode potentials. In this high-potential, strongly oxidizing environment, noble metal catalysts undergo dissolution, migration, and agglomeration, while carbon supports experience electrochemical oxidation corrosion, resulting in a sharp decrease in catalyst active area and a decline in battery performance.

To improve catalyst corrosion resistance, researchers have attempted to use antioxidant supports. However, these supports have poor conductivity, limiting power density. While introducing protective coatings directly onto the catalyst surface can improve stability, their dense structure often hinders proton transport in the low-potential region where the fuel cell operates normally. Therefore, developing a structure that can effectively protect the core components of the catalyst under high-potential threats is crucial for the long-term stable operation of fuel cells.

Summary of the Invention

In view of the above, the invention provides a a noble metal alloy catalyst for low-temperature fuel cells and a preparation method thereof, which effectively resists high-potential oxidation and corrosion and improves catalyst stability by constructing a metal-organic coordination compound composite protective layer in situ.

The technical solution provided by the invention is as follows:

The first aspect, the invention provides a noble metal alloy catalyst for low-temperature fuel cells, characterized by comprising: a conductive carrier, a catalytically active component, and a composite protective layer;

the conductive carrier is at least one selected from carbon black, carbon nanotubes, graphene, mesoporous carbon, titanium carbide, and titanium nitride;

the catalytically active component comprises noble metal alloy nanoparticles supported on the conductive carrier;

the composite protective layer is formed of a metal–organic coordination compound and is coated on the surface of the noble metal alloy nanoparticles.

Further, the noble metal alloy nanoparticles comprise either a platinum–nickel alloy or a platinum–cobalt alloy.

Further, the metal–organic coordination compound comprises a metal ion M and an organic ligand L; the metal ion M is at least one selected from cerium, zirconium, manganese, and tin; the organic ligand L is at least one selected from citric acid and ethylenediaminetetraacetic acid (EDTA).

The second aspect, the invention provides a method for preparing the noble metal alloy catalyst for low-temperature fuel cells mentioned hereinabove, characterized by comprising the following steps:

S1. loading of the catalytically active component

the conductive carrier is dispersed in a solvent to form a suspension, and a noble metal salt is added; after heating and refluxing, centrifuging, washing, and vacuum drying, an annealing treatment is performed to obtain an initial catalyst having noble metal alloy nanoparticles supported on the conductive carrier;

S2. in-situ construction of the protective layer

the initial catalyst obtained in step S1 is dispersed in a solvent, followed by the addition of a metal ion M salt solution and an organic ligand L; the pH of the system is adjusted to 5.8–6.4, and the mixture is stirred at 50–90°C for 1–4 hours to allow the metal ion and the organic ligand to coordinate on the surface of the noble metal alloy nanoparticles to form the composite protective layer;

S3. post-treatment

the reaction product is cooled, separated, washed, and vacuum-dried to obtain the noble metal alloy catalyst.

Further, the noble metal salt in step S1 is at least one selected from chloroplatinic acid, platinum nitrate, nickel chloride, nickel nitrate, cobalt chloride, and cobalt nitrate; and the mass ratio of the conductive carrier to the noble metal salt is 1:(0.1–0.5).

Further, the metal ion M salt solution in step S2 is at least one selected from chlorides, nitrates, or chlorates corresponding to the metal ion M; and the molar ratio of the metal ion M to the organic ligand L is 1:(1–3).

Beneficial effects of the invention:

The noble-metal alloy catalyst prepared according to the invention is constructed in situ with a composite protective layer formed from a metal–organic coordination compound. This protective architecture is capable of safeguarding the noble-metal alloy nanoparticles from dissolution, migration, and agglomeration under the high-potential and strongly oxidizing environment encountered in low-temperature fuel cells. It also prevents electrochemical oxidative corrosion of the carbon support, thereby markedly improving the stability of the catalyst.

Specific Embodiment of the Invention

To make the objectives, technical solutions, and advantages of this invention clearer, the technical solutions of this invention will be clearly and completely described below in conjunction with the embodiments of this invention. Obviously, the described embodiments are only some embodiments of this invention, not all embodiments. It should be noted that, unless otherwise specified, all chemical reagents involved in this invention are purchased through commercial channels.

Embodiment 1

This embodiment provides a method for preparing a noble-metal alloy catalyst for use in a low-temperature fuel cell, comprising the following steps:

S1. loading of the catalytically active component

first, 150 mg of conductive carbon black is weighed and dispersed in 80 mL of ethylene glycol; the dispersion is ultrasonicated in an ice–water bath for 1 hour to form a uniform suspension; under continuous stirring and ice-bath cooling, 20 mL of an ethylene-glycol solution containing 100 mg of chloroplatinic acid and 54 mg of nickel chloride is added dropwise into the suspension, followed by continued stirring for 30 minutes; the mixture is then transferred into a three-neck flask, heated from room temperature to 200°C at a rate of 5°C/min, and subjected to a reflux reaction for 4 hours; after completion of the reaction, the mixture is cooled to room temperature and centrifuged to collect the solid product; the collected solid is washed three times with ethanol and deionized water, respectively, and finally dried under vacuum at 60°C for 12 hours to obtain a Pt–Ni-loaded catalyst precursor; the precursor is annealed at 500°C for 1 hour under a 5% H_2/Ar mixed-gas atmosphere to obtain platinum–nickel alloy nanoparticles uniformly formed on the carbon black (denoted as the PtNi/C catalyst); the loading of the Pt–Ni alloy is approximately 20 wt%, and the alloy nanoparticles have an average size of about 4 nm;

S2. in-situ construction of the protective layer

an amount of 100 mg of the PtNi/C catalyst obtained above is weighed and ultrasonically dispersed in 50 mL of deionized water for 30 minutes to form a uniform suspension; under continuous stirring, 5.0 mL of an ammonium cerium nitrate aqueous solution having a concentration of 0.1 mol/L and 7.5 mL of a monohydrate citric-acid aqueous solution having a concentration of 0.2 mol/L are sequentially added; the pH of the system is then adjusted to 6.0 ± 0.1 using 1 mol/L aqueous ammonia; the reaction mixture is heated to 60°C and maintained for 2 hours, allowing cerium ions and the citric-acid ligand to coordinate and assemble on the surface of the Pt–Ni alloy nanoparticles, thereby forming a Ce–citrate composite protective layer;

S3. post-treatment

after the reaction mixture is cooled, centrifugation is performed to separate the solid precipitate; the precipitate is washed three times with deionized water and twice with anhydrous ethanol by centrifugation, and then dried at 60°C under a vacuum of –0.1 MPa for 8 hours to obtain the Ce–citrate-protected PtNi/C catalyst.

A high-potential cycling stability test is conducted on the catalyst prepared in embodiment 1. The test is performed in a potential window of 1–1.5 V. The results show that the electrochemical surface area of the catalyst remains essentially unchanged after 10,000 cycles. After 50,000 cycles, the electrochemical surface-area loss is less than 20%, and the half-wave potential decreases by only 8 mV. The results demonstrate that the catalyst exhibits excellent high-potential anti-corrosion stability.

The invention and its embodiments have been described above. This description is not restrictive. The embodiments shown are only one of the embodiments of the invention, and the actual structure is not limited thereto.