Study on Oxygen Reduction Method of Phosphorus-doped Hydrogenated Nano-silicon

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Abstract. In recent years, hydrogenated nano-silicon has attracted much attention due to its high specific energy density. However, the slow kinetic oxygen reduction reaction (ORR) and oxygen evolution reaction (ORE) reduce the efficiency of hydrogenation of nano-silicon and hinder its practical application. The development of non-precious catalysts with excellent performance and low price is of great significance to the development of hydrogenated nano-silicon. Among many hydrogenation nano-silicon catalysts, cobalt-based compounds have good ORR and ORE catalytic performance, and are rich in Co reserves and low in price. Especially doped compounds have excellent stability. In the thesis, three series of hydrogenated nano-silicon composite materials of Co-SrCO3/NC, Co-Nd/NC and Co-Ce/NC were successfully synthesized through heating reflow method and subsequent high-temperature calcination. XRD, Raman, XPS, TEM, nitrogen isothermal adsorption and desorption and other analytical methods were used to characterize the structure of the above composite materials. Through chemical tests, the composite materials were evaluated for the catalytic performance of ORR and ERR, and their structure-activity relationship was analyzed. The Co_SrC03/NC series composite materials were calcined at different temperatures. The results showed that the generated SrCO3 nanorods were embedded in the graphite shell and contacted with hydrogenated nano-silicon. In an oxygen-saturated 0.1MKOH solution, Co-SrC03/NC series composites have excellent ORR/ORE catalytic activity, especially Co-SrC03/NC-600 has more stable activity than precious metal catalysts of 20wt% Pt/C and Ir02. Sex. The air prepared with Co-SrC03/NC-600 has better performance. During the in-depth study of 10mA cnT2, Co-SrC03/NC-600 was used as the air to maintain a stable platform of 1.10V, and the platform of 20wt%Pt/C under the same conditions was 1.17V.

1. INTRODUCTION

Use A4 paper size (210 x 297 mm) and adjust the margins to those shown in Table 1. The final printed area will be 172 x 252 mm. With the growth of population and the rapid development of global economy, the use of energy by human beings is increasing, resulting in a rapid reduction in the storage of fossil fuels, and also causing various harmful gases to be discharged into the atmosphere, triggering a serious energy crisis and environment Question m. The development of high-efficiency, low-cost, environmentally friendly clean energy can greatly alleviate the crisis caused by energy shortages and reduce the emission of harmful substances. At present, the clean energy we can use is solar energy, etc. Its advantages are renewable, large energy, and green environmental protection. However, these clean energy sources also have shortcomings, such as intermittent, regional, etc., which will lead to the inefficient use of clean energy[1-2]. Converting the above-mentioned clean energy into electric energy that can be used stably and directly by humans, and being able to use clean energy efficiently, is one of the effective ways to alleviate the current situation. After reading a large amount of literature, we
found that many high-efficiency energy storage and conversion devices have become one of the popular researches of researchers, such as metal-air batteries, metal-ion batteries, and fuel cells. The above-mentioned energy storage and conversion device can directly convert chemical energy and electric energy, and play or will play an extremely important role in the efficient use of various clean energy sources. The metal-air battery has the advantages of high theoretical specific energy density, stable charging and discharging voltage, low price, small size, light weight and environmental protection, etc, and has been rated as a new type of green energy storage and conversion device with great development potential. According to the difference of the negative electrode metal of the battery, it can be divided into zinc-air battery, magnesium-air battery, lithium-air battery, aluminum-air battery and sodium-air battery. A large number of studies have shown that among the widely used alkaline electrolytes, only metal zinc electrodes can maintain high corrosion resistance, and metal zinc has many resources in the earth's crust, which is affordable and environmentally friendly. Through experiments and calculations, it is found that for zinc-air batteries, the theoretical specific energy can reach 1,350 Wh kg⁻¹, and the actual specific energy is about 350-500 Wh kg⁻¹, which is 2-3 times that of the currently widely used lithium-ion batteries. These advantages make zinc-air batteries pay close attention to, and become one of the hottest researches in energy storage and conversion devices. However, the commercialization of zinc-air batteries also has certain bottlenecks, that is, its high charge/discharge overpotential and poor charge/discharge performance, which makes zinc-air batteries have very low cycle efficiency and extremely limited service life. The most important reason for this bottleneck is that the two core reactions in the charging and discharging process of the zinc-air battery are extremely slow reactions in reaction kinetics. During the charging process, the oxygen electrode will lose electrons, and the oxygen evolution reaction (Oxygen Evolution Reaction, ERR) occurs; during the discharging process, the oxygen electrode can obtain electrons, and oxygen reduction reaction occurs.

Points important. Oxidation-reduction reaction (ORR) and oxidation-precipitation reaction (OER) are the core reactions of the above-mentioned energy storage and conversion devices. However, both ORR and OER reactions are processes with relatively slow kinetics, which will reduce the reaction process and reaction efficiency of the above-mentioned devices. Therefore, a catalyst with dual functions of ERR/ORR is needed to speed up the reaction process. As we all know, some catalysts have excellent ORR or ERR catalytic performance. However, the high cost greatly limits its commercial development. The catalyst has the advantages of low cost and abundant resources, and it is possible to find a very ideal substitute for the catalyst. Cobalt-based compounds are a kind of ORR and OER catalysts with development prospects, and are considered to be substitute products for catalysts. In addition, nitrogen-doped carbon materials also exhibit excellent catalytic performance. The cobalt-based compound and the nitrogen-doped carbon material are combined to obtain the hydrogenation nano-silicon catalyst, which can further improve the catalytic activity and stability of the hydrogenation nano-silicon. Zhang et al. prepared a Co/N-C composite material (named SUCo-0.03-800) and doped nitrogen into hydrogenated nano-silicon. Through the activity test, SUCo-0.03-800 has ORR activity comparable to commercial Pt/C, and has excellent stability and selectivity. This is mainly due to the difference between the nitrogen-doped hydrogenated silicon nanoparticles and Co nanoparticles. The synergy effect. Sun et al. prepared a three-dimensional porous carbon (Co-N-OMMCs) doped with Co and nitrogen by a simple double template method. Through the electrochemical test, the ORR half-wave potential of Co-N-OMMCs is 0.83 V (vs. RHE), which improves the 4 electron pathway of reaction and promotes the ORR process. In addition, it also exhibits excellent stability and methanol stability better than commercial Pt/C. Strontium carbonate (SrCO3) is an important industrial reagent, such as a glass additive for color television tubes and a composition for small DC motors using sub-ferrite magnets. In addition to the above industrial applications, SrCO3 is also used in the field of catalysis due to its structure, thermal stability and high selectivity. Zhang et al. found that the nano-sized SrCO3-based chemiluminescence sensor showed resistance to ethanol but not other substances (such as gasoline, ammonia and hydrogen).
2. ANALYTICAL METHOD

Figure 1 is the XRD diagram of the comparative samples SrC03/NC-600 and Co/NC-600 and the prepared Co-SrC03/NC-500, 600 and 700 composites at different temperatures. The diffraction peak (20) is at 25.0°, 25.6°, 29.6°, 31.3°, 36.2°, 41.4°, 44.1°, 45.7°, 47.6°, and 50.0°. When it appears, mainly SrC03 (PDF#05-0418). The diffraction peaks (20) appear at 44.2°, 51.5°, and 75.9°. When the metal cobalt (PDF#15-0806) is mainly face-centered cubic (fcc), the diffraction peaks appearing at 41.5°, 47.4°, and 75.9° are hexagonal close-packed (hcp). Metal cobalt (PDF#01-1278). As a sample, SrC03/NC_600 mainly includes SrCO3, and Co/NC-600 mainly includes fcc Co and hcp Co. The diffraction peaks of Co-SrCO3/NC-500, 600 and 700 composites prepared at different calcination temperatures are SrCO3, fcc-type Co and hcp-type Co, and as the calcination temperature increases, the diffraction peaks The intensity gradually increases. Raman spectroscopy confirmed the existence of carbon in Co_SrCO3/NC series composite materials and comparative samples. Two typical Raman peaks usually appear in the Ram of carbon materials, namely D peak and G peak.

![Figure 1 Oxidation analysis](image)

The D peak appears at the 1343 em1 Raman shift, which is caused by the lattice defects of carbon atoms, and the G peak appears at the 1580 cm Raman shift, which is caused by the carbon atom sp2 hybrid stretching vibration. Under normal circumstances, the ratio of peak intensity between peak D and peak G (Id/Ic) is used to judge the degree of graphitization of carbon materials and the degree of integrity of the graphite structure. The ID/IG values of Co_SrCO3/NC-500, Co-SrCO3/NC-600, Co-SrCO3/NC_700, Co/NC-600 are 1.16, 1.01, and 0.81, respectively. 0.87 and 0.89. After the introduction of SrC03, the ratios of Co_SrCO3/NC-500, Co-SrCO3/NC-600 and Co-SrCO3/NC-700 are increasing, but the ID/IC value of Co-SrCO3/NC-600 is the smallest. It has the least carbon defects.

3. Calculation method

The oxidation-reduction reaction is a chemical reaction in which the oxidation number of the element has a corresponding rise and fall before and after the reaction. A chemical reaction in which the valence of an element changes during the reaction is called a redox reaction. This reaction can be understood as consisting of two half reactions, namely oxidation reaction and reduction reaction. Such reactions obey the conservation of charge. In the oxidation-reduction reaction, oxidation and reduction must proceed in equal amounts at the same time. The two can be compared to the mutual dependence, transformation, ebb and flow of yin and yang as well as mutual opposition. Redox reactions also exist in organic chemistry.

For the oxidation-reduction reaction, first express the measurement number of the substance whose element valence changes more with an unknown number, and then use the conservation of mass to
balance the measurement number of other substances. Finally, the measurement number of each substance is balanced out, according to a certain The conservation of these elements is solved by equations:

- Step1: Analyze the rise and fall of chemical prices;
- Step2: Exchange the coefficient of the price increase;
- Step3: Cross the bridge (two-wire bridge);
- Step4: Find the elements that do not participate in the redox reaction and add them to the coefficient. In addition to (oxygen, hydrogen);
- Step5: Balance the hydrogen;
- Step6: Check if the oxygen is level;
- Step7: Perfect (add reaction conditions, add equal sign, add down arrow, round common divisor).

In the oxidation-reduction reaction, the following general laws mainly include:

1. Law of strength and weakness: oxidizing: oxidant>oxidation product; reducing: reducing agent>reduction product.
2. The law of valence: the element is in the highest valence state, only oxidizing; the element is in the lowest valence state, only reductive; in the middle valence state, it is both oxidizing and reductive.
3. Transformation law: When a neutralization reaction occurs between different valence states of the same element, the oxidation number of the element is only close and does not cross, reaching the same valence state at most.
4. Priority law: For the same oxidant, when there are multiple reducing agents, it usually reacts with the most reducing agent first.
5. Conservation law: The number of electrons obtained by the oxidant is equal to the number of electrons lost by the reducing agent.

Oxidation-reduction reaction (also known as redox reaction) is a type of reaction in which the valence of elements changes before and after a chemical reaction. The redox reaction is characterized by the rise and fall of element valence, which is essentially the gain or loss of electrons or the deviation of shared electron pairs. Redox reaction is one of the three basic reactions in chemical reactions (the other two are (Lewis) acid-base reactions and free radical reactions. Combustion, respiration, photosynthesis in nature, chemical batteries in production and life, metal smelting), Rocket launches, etc. are closely related to redox reactions. The study of redox reactions is of great significance to the progress of mankind. Redox reactions are divergent reactions, neutralization reactions and other types. Disproportionation reactions refer to the same element in the reaction from one valence State into two valence states. One high valence state and one low valence state, which means that the same substance acts as both an oxidant and a reducing agent. (For example, the reaction of NO2 and water, or the reaction of Cl2 and water) The centralization reaction refers to The different valence states of the same element rise or fall to adjacent valence states. But pay attention to the principle that the valence cannot be crossed. The substitution reaction must be an oxidation-reduction reaction, and the decomposition reaction and compound reaction with elemental formation are also oxidation-reduction reactions and metathesis reactions. It must not be an oxidation-reduction reaction. What is produced from a simple substance is not necessarily an oxidation-reduction reaction. Allotropes are not. For example, graphite (C) chemically reacts under high temperature and pressure to produce diamond (C), and the valence has not changed, so it is not a redox reaction.

The oxidation-reduction reaction of hydrogenated nano-silicon is also related to polysilicon. Due to differences in structure, crystalline ratio, grain size, preparation methods, etc., there are other crystalline-amorphous two-phase mixed silicon materials, which are introduced as follows: Poly-Si (poly-Si) generally refers to crystalline state For a mixed-phase system with a ratio greater than 90%, the silicon crystal grains are on the order of micrometers, and the crystal grains are in disordered interface regions; there is no essential difference between the band structure and single crystal silicon, but there are a large number of defect states in the interface region. Affect the nature of electrical...
Transport. Hydrogenated microcrystalline silicon (μc-Si:H) is not strictly distinguished from nc-Si:H in the international arena. It refers to a single crystal-amorphous mixed phase system with a grain size in the range of several nanometers and micrometers. Domestic Chen Hong believes that the main difference between μc-Si:H and nc-Si:H is the difference in grain size. The crystal grains of nc-Si:H are a few nanometers, and the crystalline ratio is about 50%; while the crystal grains of μc-Si:H are larger, and the crystalline ratio is generally lower than that of polysilicon. The transition region between a-Si:H and μc-Si:H is polymorphic silicon (pm-Si:H) or protocrystalline silicon (proto-Si:H). These two materials have more stable optoelectronic properties than a-Si:H. Their amorphous silicon network

There are nano-scale silicon crystal grains, but the crystal grains are sparse and the crystalline ratio is less than 10%. The main difference between the two comes from the difference in the preparation process. Porous silicon (porous silicon) is a complex system with Si, O, and H elements coexisting in composition; microcrystalline, amorphous, and pores coexist in structure; porous and sponge-like, richer than the surface, and complex in the interface state. Porous silicon generally uses crystal

Bulk silicon or amorphous silicon is obtained by anodic oxidation, dye corrosion, spark discharge and photo-assisted chemical corrosion in hydrofluoric acid, and the anodic oxidation method is currently the most important method for preparing porous silicon. Porous silicon can emit effective visible light at room temperature and is a new type of visible light luminescent material, which is very attractive to people. There are other silicon nanostructure materials, such as silicon nanocrystals embedded in the network of amorphous SiO2 or silicon nitride, etc., which are not specifically explained here.

The oxidation-reduction reaction of hydrogenated nano-silicon is also related to physical deposition. Physical vapor deposition (PVD) refers to the use of certain physical processes, such as the thermal evaporation of substances or the use of particle beams

Phenomena such as the sputtering of atoms on the surface of the substance during the bombardment realize the controlled atomic transfer process of the substance from the source substance to the film. Compared with the chemical vapor deposition method, this method has the following four characteristics:

1. Need to use solid or molten material as the source material for the deposition process;
2. The source material enters the gas phase through a physical process;
3. A relatively low gas pressure environment is required;
4. No chemical reaction occurs in the gas phase and on the surface of the substrate.

4. CONCLUSION

The application of the oxidation-reduction reaction of hydrogenated nano-silicon has a certain degree of reliability and good practical value. It has a certain promotion effect. At the same time, it has a good application effect in real life.

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