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Application of metal-based nanomaterials in lithium batteries

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Abstract. Due to the current lithium-ion battery performance there are still many deficiencies, battery performance needs to be improved, so people through the synthesis of metal-based nanomaterials, and its application in lithium batteries to improve the electrochemical performance of batteries. This paper summarizes the application of some metal nanomaterials in lithium batteries, such as silver, platinum and gold. These metal nanomaterials can not only be used in the positive electrode as a supported catalyst to solve the problems of low charge and discharge overpotential, insufficient battery capacity, and unstable cycle performance, but also can be used in the anode. Among them, TiO_2 nanoparticles used in the anode can enhance lithium ion diffusion and charge transfer, which can provide higher battery capacity, rate performance and cycle stability for lithium batteries. Lithium batteries are expected to become a new generation of all-round use of energy in the future, not only because it is significantly less than the traditional fuel cell pollution to the environment, lithium batteries also have a higher performance limit than fuel cells, so how to improve the capacity of the existing lithium batteries, cycle stability and other performance is the direction that people need to study.

Keywords: Lithium Batteries, Metal Nanomaterials, Application.

1. Introduction

With the rapid development of human progress and global science and technology, batteries have become a very important and indispensable industry in people's modern life, and lithium-ion batteries are the most widely used in all batteries, mainly used in hydropower, thermal power generation, wind power and solar power and other energy storage systems, as well as electric bicycles, electric vehicles, special equipment, special aerospace and so on. As far as our nation is concerned, car pollution is getting worse and worse, and the damage caused by fuel vehicle exhaust, noise, and other environmental pollution is also getting worse and worse, especially in some cities with high population density, better economic development, and traffic congestion. This situation cannot be ignored, and lithium-ion battery electric vehicles, with their pollution-free, low pollution, energy diversification, and other characteristics, in the electric vehicle industry has been vigorously developed. Therefore, using lithium-ion batteries to solve the existing issue is a fantastic idea [1].

However, with the update of battery application related products, people's requirements for batteries are getting higher and higher, the current commercial lithium-ion battery commonly used anode material is graphite, but due to its low theoretical capacity, it is obvious that for the current industrial requirements of research and industrial renewal iterations, lithium-ion batteries in traditional industries have been difficult to meet. Therefore, a new challenge in the field of contemporary electrochemistry is how to enhance the electrochemical properties of lithium-ion batteries.

The application of nanomaterials makes it possible to enhance the performance of lithium-ion batteries, and the use of nanomaterials can improve the energy density, cycle life and safety capabilities of lithium-ion batteries, which brings new opportunities and challenges for the development of lithium-ion batteries [2]. Nanomaterials can be divided into precious metal nanomaterials, non-precious metal nanomaterials and composite nanomaterials, where precious metal-based nanomaterials are widely used and their main use is as a high-efficiency catalyst in batteries. For example, platinum, palladium, ruthenium, iridium, osmium, gold and other precious metals have good catalytic activity, stability and anti-toxicity, so they are widely used in catalytic reactions. So far, precious metal nanomaterials can be divided into three types: precious metal elemental and compound nanopowder materials, precious metal new atomic clusters and precious metal film materials, of which precious metal elemental and compound nanopowder materials can be divided into two types: supported powder materials and non-supported powder materials, which are the most used precious metal-based nanomaterials in industry. The precious metal nanomaterials we discussed that can be used as efficient catalysts belong to the supported precious metal nanomaterials, which usually refers to the complex obtained by loading the nanoparticles of precious metals and their compounds onto a certain porous carrier, and it is also known as the precious metal composite nanomaterials, which has two major advantages: First, it can obtain dispersed and uniform precious metal elemental and compound nanomaterials, effectively preventing the polymerization of precious metal nanoparticles; Second, the production process is simpler than other precious metal nanomaterials, and the technical indicators are easy to control. In terms of its application, due to the small particle diameter of the material, the specific surface area increases, and the valence of the element is seriously unbalanced, so unsaturated bonds appear, so that the overall number of active sites on the precious metal nanoparticles' surfaces increases, showing high activity, and it is easy to adsorb other atoms and catalyze chemical reactions with high efficiency. In addition, the unique chemical stability of precious metals.

Metal nanomaterials have unique catalytic stability, catalytic activity and regeneration after being made into catalysts. Therefore, the supported metal-based nanomaterials are expected to become a new generation of efficient catalysts, which can directly convert chemical energy into electricity, the catalytic efficiency is even higher than that of thermal power generation, it is not limited by the Carnot cycle, and the energy conversion rate is very high, while it does not produce sulfur oxides and nitrogen oxides, and carbon dioxide emissions are correspondingly reduced. At present, there are many kinds of high-efficiency nano-scale metal catalysts that have been applied in industrial production, such as colloidal Pt catalyst on zeolite for converting alkanes into petroleum, colloidal Ru on carbon for ammonia synthesis, and Pt100-xAux colloidal for hydrolysis and isomerization of n-butane. The commercialization of fuel cells depends substantially on nanomaterials made of valuable metals, particularly Pt composites, as 1-10 nm Pt particles have excellent catalytic performance, fuel cell catalysts made of Pt nanomaterials can not only improve its catalytic performance, but also reduce the amount of precious metals, resulting in a significant reduction in preparation costs. To achieve a wider range of industrial production conditions. In this paper, it will discuss the effect of nano-synthetic materials of ruthenium, palladium, silver, platinum, gold, tin, titanium and other metals used as catalysts in lithium batteries, and find that the performance of lithium-ion battery can be effectively improved by the addition of metal nanocatalysts.

2. Application of different metal nanomaterials in lithium batteries

A diverse of different metal-based nanomaterials has been synthesized, such as ruthenium, palladium and silver, and can be used for the preparation of the positive electrode of lithium-oxygen batteries and show an increase in battery performance. In addition to their potent catalytic activity, metal nanocatellites also exhibit chemical characteristics including resistance to oxidation, corrosion, and high temperatures, which have important applications in the field of electrocatalysis. Here, the application of different metal nanomaterials in batteries will be systematically analyzed.

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2.1. Ruthenium-based catalysts

The use of ruthenium (Ru) nanoparticles as catalysts can catalyze the strong REDOX reaction and oxygen evolution reaction in lithium-oxygen batteries. The use of ruthenium nanomaterials mixed with carbon materials as the positive catalyst of lithium oxygen battery can greatly reduce the overpotential during the charge and discharge process of lithium oxygen battery, and then improve the cycle performance of lithium oxygen battery. At the same time, the specific surface area of ruthenium nanoparticles is large and the particles are highly dispersed, which is conducive to the formation of the active site of the positive catalyst, and the support of ruthenium also improves the dispersion of discharge products, adjusts their particle size, and prevents their excessive growth, which can provide enough space for discharge products, promote the diffusion of oxygen and electrolyte, and reduce overpotential. Due to the interaction between ruthenium nanoparticles and carbon matrix interface, ruthenium particles transfer electrons to carbon groups, improve the surface adsorption energy of reactants and intermediates, and then improve the electrochemical performance of lithium-oxygen batteries, which can make its stable cycle 300 times, can reach 25632 mAh/g discharge specific capacity [3].

For example, RuO_2-Co_3O_4 nanohybrid, a catalyst with oxygen-rich vacancy and large specific surface area that can reduce the overpotential of lithium-oxygen batteries, can be prepared by sol-gel method of Ru-oxide-modified boron-doped multilayer porous reduced graphene aerogels and used as oxygen electrodes [3]. The prepared three-dimensional porous nanogel has a large specific surface area and mostly porous structure, which can provide sufficient storage space for Li_2O_2 formed during discharge, while the exposed RuO_2 particles can effectively catalyze the reaction of the electrode.

2.2. Palladium-based catalysts

Palladium (Pd) nanoparticles are also widely used in lithium batteries. The addition of palladium-based catalyst has a significant effect on the formation of Li_2O_2, the discharge product on the positive electrode of the battery. A porous carbon material with a super-polar surface is used as the substrate, and PdO-Co_3O_4 nanododecahedron modified with Pd on the substrate is used as the efficient catalyst for lithium-oxygen batteries [4]. Not only can reduce the overpotential during charging and discharging, but also enhance the reversibility of strong REDOX reaction and oxygen evolution reaction, through the layer structure combined with highly dispersed active particles, effectively improve the performance of the battery, so that the battery can be stably cycled more than 90 times, greatly extending the cycle life, and improving the catalytic performance of the catalyst material.

Pd-based catalysts are more based on carbon-based materials, and Pd nanoparticles are modified on the substrate. For example, by interfacial spontaneous REDOX method, doped Pd converts the 2H phase of MoS_2 semiconductor into a stable metal 1T phase, and a new 1T-MOS_2 nanosheet array is obtained as an independent positive catalyst [3]. Its electronic structure enables the electrode to increase the power and electron transfer rate of the reaction, and also catalyzes the generation of the active site, thus significantly improving its intrinsic catalytic behavior in lithium-oxygen batteries.

2.3. Silver-based catalysts

Silver (Ag) nanoparticles have the advantages of mild chemical reaction conditions and good electrical conductivity. In lithium-oxygen batteries, silver nanoparticles can improve the conductivity of oxygen electrodes, and silver nanoparticle composites can also increase the specific discharge capacity of lithium-oxygen batteries, reduce the gap between charging and discharging, and improve the cycle life of lithium-oxygen batteries. Silver nanoparticles attached to the positive surface of the battery can change the bond energy of the compounds that undergo electrochemical reactions, thus providing targeted catalysis and providing more active sites, providing a continuous channel for oxygen and discharge products.

The design and synthesis methods of Ag-based catalyst materials are mainly precipitation method and hydrothermal method. The $Ni_xAl_yMn_zO_2$ polymetallic oxide synthesized by precipitation method can be used as a dual-function catalyst for high-performance lithium-oxygen batteries and air electrodes [3]. The silver covered on the surface can change the bond energy of reactants, so as to catalyze some special chemical reactions. Ag-MnO_2 nanowires with layered porous structure prepared by hydrothermal method are thicker and have mesoporous and microporous layered structures.

2.4. *Iridium-based catalysts*

The composite catalyst material formed by the coating is easy to produce synergistic effect in lithium-oxygen battery, which can enhance the catalytic activity of the electrode and improve the reversibility of the battery reaction. The use of Ir clusters to study positive electrode materials that help control the formation of superoxide lithium during discharge has the good electronic conductivity required for low charge potential, and the synergy between Ir coatings and batteries can effectively mitigate unnecessary reactions and improve the reversibility of lithium-oxygen batteries by regulating the production of Li_2O_2. Pt has strong electrocatalytic activity to the cathode reaction of lithium oxygen battery and can be used as the nucleation site of Li_2O_2 growth. The addition of Au nanoparticles not only improves the conductivity of the electrode, but also provides an additional catalytic nucleation site for the growth of Li_2O_2 during the discharge process, which improves the catalytic activity, so that Li_2O_2 is uniformly formed and the polarization effect during the cycle is reduced.

2.5. *Composite metal catalysts*

The low-load Au-Pd alloy decorated carbon fiber positive catalyst prepared by magnetron sputtering method can be used as the material for catalyzing the cathode of lithium oxygen battery. The composite material not only improves the activity of the cathode catalyst, but also makes it have better electrochemical performance. Compared with the cathode without catalyst, the specific capacity, invertibility and cycle life of the battery have been improved. Transition metal oxid-based bimetallic nanocomposites (Pt-Ir/C-TiO_2) prepared by wet impregnation method were composed of uniformly dispersed nanoparticle alloys. Electrochemical characterization showed that Pt-Ir/C-TiO_2 electrocatalysts had dual functions and showed high activity to both ORR and OER [3].

Lee et al. successfully used specialized clones and multipurpose clones to synthesize high aspect ratio pure Ag and Au precious metal nanowires and their alloys with diameters less than 50 nm, which can effectively improve electrochemical energy storage capacity [5]. Excellent surface activity additionally remains evident, small diameter nanowires can also alleviate the stress caused by large volume changes during lithium ionization and shorten the diffusion distance of Li. The unique clone virus encodes a gold-binding peptide motif on the primary coat protein, which is employed to construct gold nanoparticles and has a specific affinity to both gold ions and gold atoms. In addition to bioscanning for biomolecular recognition of particular materials, the virus can also independently modify its surface function through genetic engineering. The primary coat protein of the modified M13 virus, known as the multifunctional clone virus, has tetratglutamate fused to the amino terminus on each copy. Compared to M13 viruses of the wild type, E4 viruses have more carboxylic acid groups than other viruses, which results in greater ionic interactions with cations and can serve as a template for material growth. In their experiments, nanowires made of pure gold and silver showed rapid capacity attenuation to lithium batteries, while their noble metal alloy nanowires showed good capacity retention. They speculated that the improved capacity retention in the alloy system was related to the surface stability of CTAB or the pseudo-single-phase behavior in the potential profile [5].

Ai et al. designed sub10 nm ultra-small tin-based nanoparticles to replace commercial graphite anodes by studying their presence in reduced graphene oxide hybrid or hierarchically porous carbon that is codoped with nitrogen and phosphorus [6]. The long cycle life and high rate of tin-based lithium-ion battery anodes can effectively solve the problem that tin-based anode sources are hindered by rapid capacity decay cycles due to large volume changes. In NPHPC and NPHPC-G composites, the average size of stannum microcrystals is roughly-approximately 6-8 nm, and a large number of stannum nanoparticles of uniform size are evenly dispersed in 3D macroporous structures [6]. Due to their morphological uniqueness and structural uniformity, they can not only withstand tin-based nanoparticles with huge volume changes, but also maintain the framework of the framework. Thus, the electrode material has excellent electrochemical properties. In order to create higher performance tin-based anodes,

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mainly in the synthesis of NPHPC and NPHPC-G composites, they prepared these two Sn composites by one-step in-situ carbonization of melamine polyphosphate adsorbed by tin ions in the experiment [6]. Both NPHPC@SnO_2 and NPHPC-G@SnO_2 are produced using a single hydrothermal pot [6]. Through the analysis of experimental data, it is found that these two materials exhibit better rate performance and cyclic stability, which have reached the top level of tin matrix composites. First, the ultra-small size stannum-based nanoparticles provide many active sites for the storage of lithium ions without causing any serious deterioration of the electrodes due to their nanoscale effect. At the same time, because these nanoparticles are closely arranged on the carbon matrix, they can effectively limit the movement of tin, so the phenomenon of blocky tin clusters in the process of alloying and dealloying can be inhibited. Second, the carbon-based frame with high hardness and conductivity not only enables rapid electron transmission, but also contributes to keeping the composite electrode's structural integrity. Third, the special structure of the NPHPC is conducive to increasing the final capacity of the hybrid, while the integrated graphene sheet is conducive to better confining the tin-based nanoparticles, while also providing power for rapid electrochemical reactions of lithium ions and electrons.

Zeng et al. prepared single-layer TiS_2 and TaS_2 nanosheets and demonstrated that Pt and Au nanoparticles grow on TiS_2 and TaS_2 nanosheets to form functional composites [7]. Through experiments, TiS_2 and TaS_2 are examples of monolayer metal disulfide that they prepared and multi-layer metal selenides such as Sb_2Se_3 and WSe_2 by electrochemical lithium intercalation method, in order to minimize the shortcomings of individual components and maximize their advantages. After the formation of composite materials, there may be other effects in addition to enhancing properties. The two-dimensional nanostructures of single-layer and low-layer nanosheets and their ultra-thin thickness make them easy to be used as ideal media for constructing composite materials, and are applied in lithium-ion batteries, fuel cells, photovoltaic devices and other fields. They proposed that noble metal nanomaterials could grow outwards on monolayers of MoS_2 nanosheets that could be processed in solution under certain conditions, and Pt-MoS_2 composites showed great electrocatalytic activity in hydrogen evolution reaction [7].

Building on previous work, they optimized experimental conditions for producing monolayer TiS_2 and TaS_2 nanosheets, such as the high yields of lithium embedding and stripping methods. First, determine the value of cutting-off voltage at various potentials in order to regulate the amount of lithium ions inserted. Second, to lessen the diffusion stress caused by the lithium ions in the layered crystal, a low current is provided. Thirdly, the solution of the intercalated compound is deoxidized with saturated nitrogen to prevent the oxidation of the lithium intercalated compound during the ultrasonic process. Finally, high quality and high yield single-layer TiS_2 and TaS_2 nanosheets were successfully prepared [7]. They also observed that nanoparticles of Pt and Au with restricted size distributions were deposited on the two produced nanosheets. The experimental results show that setting lower cutting-off voltage and release current during the battery discharge, using deoxidation treatment during the ultrasonic process, and using multistage centrifugation are conducive to the single-layer TiS_2 and TaS_2 nanosheet preparation, and the gained TiS_2 and TaS_2 nanosheets can be used as a new platform for the creation of composites made of precious metals [7].

Among the many challenges faced by lithium-oxygen batteries, the electrode overpotential during charging is excessively high due to the sluggish oxygen evolution reaction rate, which is one of the causes of their low battery efficiency, Ru-rGO hybrid exhibits the most stable cycling performance and the lowest charging overpotential among precious metal nanomaterials, which can greatly lower the charging overpotential [8]. Jeong et al. studied the discharge products of Ru nanoparticles in the reaction and found that Ru nanoparticles appear to behave significantly differently than conventional electrocatalysts, which lower the activation barrier by transferring electrons, because controlling the characteristics of the discharge products is a key role that Ru nanoparticles play in lowering charge overpotential. Nanoparticles of Ru promote the REDOX reaction during the formation of Li_2O_2, causing it to decompose at a lower potential during the charging process, and the electrolyte stability is still good after catalysis with Ru-RGO hybrid. This study proves that for lithium-air batteries, the stability of the electrolyte can be ensured while selecting an electrocatalyst.

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They evaluated how well Pt, Ru, and Pd nanoparticles supported by reduced graphene oxide performed as electrocatalysts for lithium-oxygen batteries [9]. Compared with conventional carbon, using two-dimensional graphene carriers, the interaction between precious metals and functional fossil ink surface rGO is stronger, so the electrocatalyst nanoparticles are more dispersed on the rGO, and their larger surface area and porous structure also help to enhance its catalytic performance [8], as shown in Figure 1. In the experiment, they found that the noble metal nanoparticles had no effect on the discharge potential, and the charging overpotential of the three noble metal materials used in the experiment was significantly reduced, while Ru-rGO had the lowest charging overpotential and the most consistent cycling performance. Finally, they also examined the catalytic activity. Ru-rGO has an increasing current density in contrast to rGO, and the curve on the Pt-RGO electrode was consistent with constant current, indicating that Pt has less catalytic activity than Ru does. The nanoparticles of Ru selectively accelerate electrode oxidation through twofold action, according to the examination of electrolyte stability and reaction products, while Pt and Pd have no selectivity for oxidation reaction, which confirms that the industry can use specific suitable catalysts and nanoengineering to enhance lithium-oxygen battery performance.

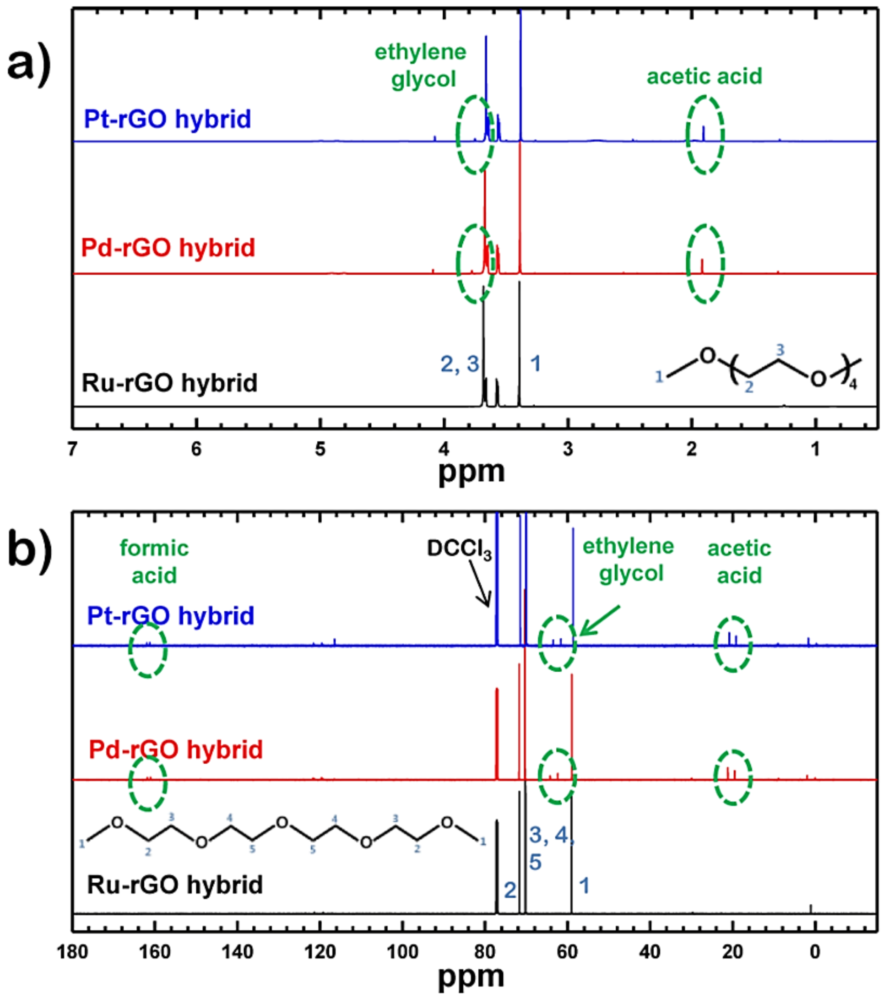

Figure 1. In (a) H and (b) C, nuclear magnetic resonance analysis of air electrode was performed using Pt-rGO, Pd-rGO and Ru-rGO composite nanocatalysts [8].

Sanad et al. successfully synthesized mesoporous TiO_2 by hydrothermal solution without the addition of template agent [10]. As shown in Figure 2, among the different TiO_2 polymorphs, anatase is generally considered to be the most electrically active host material for Li-embedding and deembedding, because the anatase structure's deformation of the [TiO_6] octahedral unit promotes thermodynamic stability and enhanced Li ion transport [10]. Between anatase particles are embedded particles of Ag, Pt, and Pd. X-ray diffraction and other characterization techniques were used to describe the sample's structural characteristics. The experimental results showed that the electronic conductivity of lithium-TiO_2 cells was significantly improved, and compared with pure TiO_2, all of the TiO_2 nanocomposites that were made using synthetic means had excellent specific capacity, cycle stability, and rate performance.

By adopting a synergistic nanofabrication process, the hydrolyzation-hydrothermal method was used to create titanium dioxide nanoparticles, and then $TiOCl_2$ solution was added to boiling deionized water to prepare a colloidal suspension of titanium dioxide. When the prepared suspension is heated at a high temperature for 8 hours, it can be noted that the doped titanium dioxide sample obtains different grades of gray, which provides a clear indication of whether the noble metal has been successfully blended. The product of heat treatment of the filter water was washed and dried at 100 ℃, and ultra-high capacity and very stable mesoporous TiO_2 nanoparticles were successfully obtained [10].

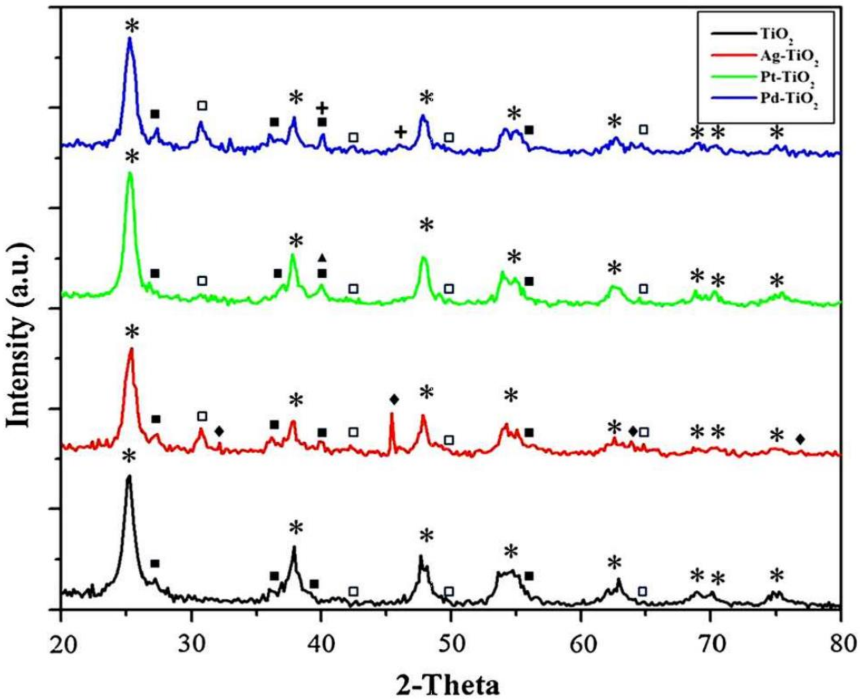

Figure 2. Anatase (asterisk), Rutile (open square), Brookite (filled square), Silver (filled diamond), Platinum (filled triangle), and Palladium (plus symbol) are the materials used to make the TiO_2 anode in their as-produced forms [10].

3. Conclusion

In general, metal nanocatalysts have higher catalytic activity and selectivity than common metal catalysts. In recent years, metal nanocatalysts such as Ru, Pd, Ag, Pt, Au, Sn and other materials have been applied to various parts of lithium batteries. The creation of active sites is encouraged by the presence of precious metals, and this activity can significantly increase the specific capacity and cycle stability of lithium batteries. Although metal nanocatalysts have good performance, because precious metals are currently scarce on Earth and very expensive, in the practical use of lithium batteries, the total number of metal catalysts is constantly constrained. Therefore, in the future lithium battery precious metal catalyst research work, people in addition to optimize the composition and structure of the catalyst, but also need to continue to improve the atomic utilization of precious metals, as far as possible to reduce the content of precious metals in the battery, while maintaining the performance of precious metal catalysts. In summary, when using precious metals as lithium battery catalysts, catalysts in the form of complex single atoms can be used, or methods to improve the specific surface area can be used to improve the utilization of precious metal atoms.

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