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Lithium Iron Phosphate Battery Resource Utilizatio

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Abstract

With the deepening of the world energy crisis and the innovation of domestic policies, lithium iron phosphate batteries are widely used in daily life. The demand for batteries has expanded one after another, and the amount of scrapped batteries has also increased dramatically. In this paper, according to the different attenuation degree of retired lithium iron phosphate battery, with 80 % and 30 % as the boundary, the recovered battery is classified, and the battery with different capacity is used step by step. When the battery capacity is 30 % -80 %, the entropy weight TOPSIS is used to select the index, and then the WOA-SVM model is used to analyze the specific performance parameters of the battery and distribute them reasonably. The battery capacity is less than 30 % for ion recovery, the cathode material is collected and used for chemical reaction.

Keywords

Lithium Iron Phosphate Battery; Entropy Weight TOPSIS; WOA-SVM; Ion Recovery; Citric Acid-ascorbic Acid System.

1. Introduction

Lithium iron phosphate battery is a popular power battery with high operating voltage, high energy density, long cycle life and high recovery rate of valuable metals. With the modern mode of high consumption and high demand, the application of lithium iron phosphate battery will gradually expand. At present, more than 30 % of domestic power battery head enterprises use lithium iron phosphate battery as cathode material, showing a rapid growth trend.

With the increasing use of lithium iron phosphate batteries, the amount of scrap is also increasing.As of 2020, the total number of retired batteries in China is about 25 GW·h (about 200,000 t), and the total echelon utilization of retired batteries is about 14 GW·h (about 140,000 t). By 2025, the cumulative decommissioning amount is about 116 GW·h (about 780,000 t), and the cumulative echelon utilization of decommissioned batteries is about 65 GW·h (about 550,000 t).The problem of recycling and utilization of retired lithium iron phosphate batteries for new energy vehicles is becoming more and more urgent. After a large number of batteries are decommissioned, it will bring safety, environmental problems and waste resources if they are not properly disposed.Therefore, it is of great significance to recycle and reuse a large number of scrapped lithium iron phosphate batteries, which not only reduces pollution, but also is of great significance to the sustainable development of the country.

2. The Wave of Power Battery Retirement Is Coming

With the increasingly serious energy and environmental problems in the world and the innovation of China 's " double carbon " policy, the number of new energy vehicles and the amount of power battery scrap are showing explosive growth.At present, the first batch of batteries in China has entered the retirement period, and the number of retired batteries will continue to grow at a high speed.This part will describe the development status of power batteries from three aspects : annual output of power batteries, scrap volume and recycling market status.

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2.1 The Annual Output of Power Battery

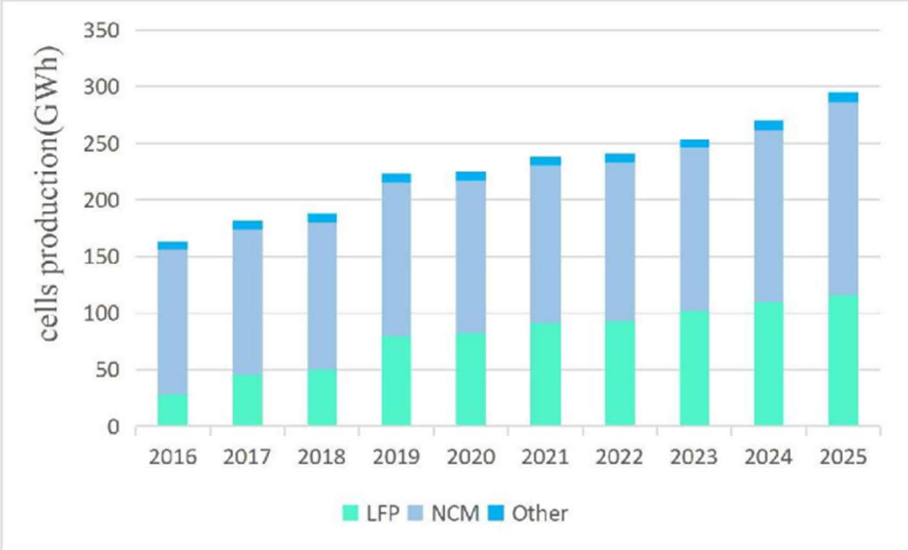

Figure 1. Forecast of China 's vehicle power battery production from 2016 to 2025

According to the data provided by the National Bureau of Statistics, drawing 1, it is not difficult to find that the production of various types of lithium batteries is increasing, the proportion of different types of batteries has changed, but the growth trend of lithium iron phosphate batteries is still strong.By 2025, the cumulative decommissioning of lithium iron phosphate is about 116 GW·h (about 780,000 t), which also indicates that China 's lithium iron phosphate battery will continue to be produced and has great recycling potential.

2.2 Waste Quantity of Power Battery

Figure 2. Prediction of vehicle power battery scrap in China from 2016 to 2025

According to the relevant index of China Renewable Resources Recycling Association, by 2022, China 's cumulative scrapped amount will exceed 10 GW·h ; it is expected that by 2025, the cumulative scrap will exceed 44 GW·h.Under the trend of rapid growth, the amount of scrapped lithium iron phosphate batteries has gradually increased. At present, the retired batteries are in urgent need of recycling, echelon utilization and other related work.

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2.3 The Current Situation of Power Battery Recycling Market

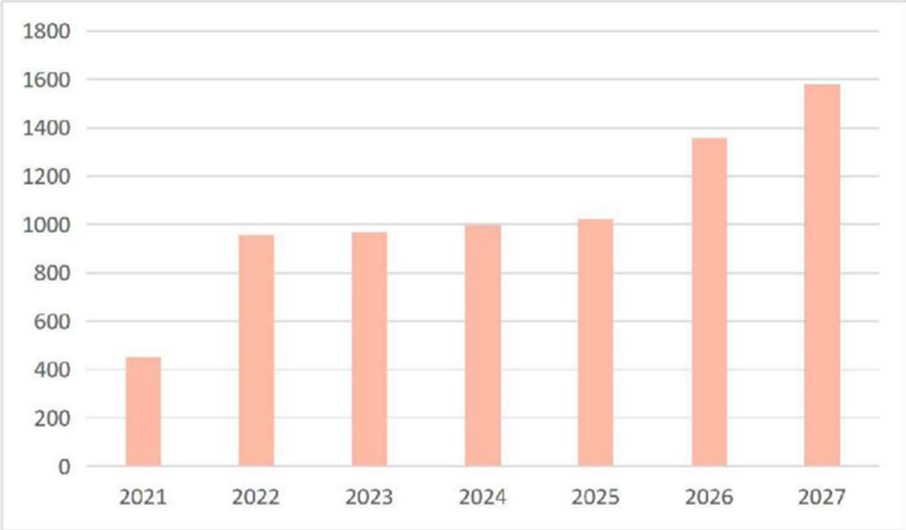

Figure 3. Prediction of the total market scale of lithium battery recycling

According to the forecast of the lithium battery recycling market by the National Information Forecasting Department, the recycling of power batteries will rapidly generate a huge emerging market, which is expected to reach 100 billion yuan by 2025.It can be seen that the recovery of power batteries, especially lithium iron phosphate batteries, contains huge market potential and technological demand.

2.4 Summary of the Development Status of Power Batteries

Power battery specifications, a wide variety, poor connectivity and interchangeability, but the demand is large, still maintained in the rising stage ; at the same time, with the update and iteration of the product, most of the batteries enter the ' retirement period ', and the problem of how to properly place these ' retirement ' batteries has also been put on the agenda and become an urgent problem.

3. Literature References

With the shortage of lithium resources and the rising price of lithium carbonate, retired batteries produce a large amount of waste. If the retired batteries cannot be properly handled, it will bring huge economic losses, waste of resources and environmental protection problems. Based on this, the state has issued a number of policies and regulations to regulate the recycling of directly retired lithium-ion batteries. Lithium battery recycling methods can be divided into : echelon utilization, direct recovery.

3.1 The Echelon Utilization and the Problems Faced at the Present Stage

After the detection and evaluation, the retired power battery can be applied to different scenarios according to the different battery status.In theory, high-capacity batteries can be used for battery replacement and energy storage applications, while low-capacity batteries can be used as backup batteries, or used in low-rate discharge scenarios such as lighting, base stations, home energy storage, UPS, charging piles, and low-speed electric vehicles.At present, the application in China mainly focuses on energy storage, base station power supply, low-speed tram and other fields. Some application cases are shown in Table 1 :

At present, the hierarchical management of echelon utilization is vague, and the manual detection efficiency of single battery is low. It is impossible to predict the change of battery charge and discharge law, and there is a lack of efficient and accurate simulation evaluation and prediction of battery performance change.

Table 1. Cases of echelon utilization of some retired power batteries in China

Application scene	Project content	The project scale
Optical storage charging station	The retired lithium iron phosphate power battery module is combined with the ' optical storage and charging ' system to build photovoltaic power generation, charging pile and energy storage system.	Energy storage with echelon utilization 0.2MW/1.1MW·h
Pumped storage plant(Peak frequency modulation)	Build a grid-side energy storage power station for the secondary utilization of new energy vehicle power batteries, and use it for peak shaving and valley filling of power load in industrial and commercial parks and provide power auxiliary services.	The total scale is about 130MW / 260MW·h, including the cascade utilization of energy storage is 75 MW·h
Communication base station	Adding retired power batteries and original backup batteries can provide a stable guarantee for the coverage of 5G signals in some areas, and improve communication security and technical economy.	The total capacity of the battery is 20 kW·h
Sanitation electric vehicle	Using retired batteries to develop low-voltage electric vehicles such as sanitation three-wheel sprinklers and street sweepers, integrating lithium battery pack BMS, cloud management platform and other functions, a echelon utilization product is developed to replace the existing lead-acid battery product.	The national cumulative capacity is about 3GW·h

3.2 Direct Recovery and the Problems Faced at this Stage

Direct recycling is to extract valuable metal elements from scrapped power batteries or power batteries after echelon utilization by physical, chemical and other recycling processes.In the pretreatment process of most lithium-ion battery recovery, NaCl solution immersion method is used. This method is suitable for discharge treatment of waste batteries due to its high discharge efficiency and low cost.However, if the battery is damaged, $LiPF_6$ contained in the electrolyte will react with water to form HF, which will cause harm to the environment and workers.Common recovery technologies include wet treatment, fire treatment, electrochemical method, co-precipitation method, hydrothermal synthesis method, solid phase regeneration, sol-gel method and so on.At present, the commonly used inorganic acid hydrometallurgical recovery system has high cost and is easy to produce harmful substances such as chlorides and nitrogen oxides to pollute the environment. It is urgent to develop green and high value-added recycling strategies.

In summary, the above problems not only affect the reasonable induction of waste batteries, but also relate to fundamental issues such as national economic development and environmental governance. Therefore, it is urgent to develop new solutions to provide efficient, convenient, low-cost, green and environmentally friendly new ideas for power battery recycling.

4. Design Scheme

Due to the physical and chemical properties of the power battery itself, its capacity will gradually decay with time[1]. When the capacity reaches 80 %, it needs to be retired from the power car. At this time, it can be used in a echelon way.

Firstly, multiple indicators are set up for various performance tests of retired power batteries, and then the system uses the entropy weight-TOPSIS algorithm to evaluate. Finally, when the battery evaluation reaches the available range, the battery is reorganized for echelon utilization. According to the capacity of the retired battery, the WOA-SVM algorithm can be used to analyze the specific performance parameters, and the reasonable allocation can be completed according to the actual situation.

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Secondly, the feedback situation is counted, so as to continue to increase to the training set of the algorithm, which is used to increase the accuracy of the test set, so as to achieve the purpose of continuously improving the allocation ability.The power battery with a capacity of less than 30 % is recycled. Firstly, the battery is deactivated by chemical reagents such as NaCl, and then disassembled, crushed and screened[2]. It is divided into metal shell, positive electrode material and negative electrode material.

The system is to recycle the cathode material, so the cathode material is mainly lithium iron phosphate after screening. Citric acid-ascorbic acid reagent is added to the system to react it into ions, and citric acid is more conducive to leaching lithium in the cathode material. Ascorbic acid reduces the Fe element in the cathode material to a low valence state for subsequent lithium precipitation[3].

The system contains lithium ions, iron ions, aluminum ions, copper ions and so on. First, carbon dioxide is introduced to precipitate lithium from the solution system, and then centrifugal treatment is carried out to divide the filtrate and filter residue, and then the lithium carbonate is filtered and washed into pure lithium carbonate. The reaction with organic solvents finally produces lithium iron phosphate[4]. Tributyl phosphate was added to the filtrate system to leach iron. After filtration, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester was added to enrich and recover aluminum ions, and aluminum ions were oxidized to alumina[5]. In the discharge deactivation of the battery, the industry usually uses the NaCl chemical discharge deactivation method. During the operation, the damaged battery may react with it to produce hydrogen fluoride gas, so the generated alumina is used to adsorb the harmful gases such as hydrogen fluoride that may be produced in the system[6].

5. Analysis of WOA-SVM Algorithm

Reasonable selection of model and algorithm parameters is the key to improve the specific performance and analysis accuracy of lithium iron phosphate battery. Since the standard support vector machine belongs to the binary classifier, this study uses a one-to-one method to realize the echelon classification of lithium iron phosphate battery.There are two algorithm parameters to be optimized in the support vector machine here : penalty parameter C and kernel parameter γ. This study uses WOA to deeply optimize the two algorithm parameters that constitute the search agent $x_{ij}^t = (x_1{}^t{}_j , x_2{}^t{}_j) = (C_i , \gamma_i)$. $X(t) = (x_1{}^t{}_j , x_2{}^t{}_j , x_{ij}^t)$ is the ith dimension of the ith agent, and t is the current number of iterations.

The parameter optimization process of WOA-SVM model for capacity performance analysis of lithium iron phosphate battery is shown in Figure 4. The search agent $x_{ij}^t = (C,\gamma_i)$ in WOA contains the optimized model parameters in SVM algorithm[7].

In the parameter optimization process of the WOA-SVM model, only the training data set is used. In addition, a five-fold cross-validation method is used to obtain the fitness value of each search agent.

Firstly, the training data set is randomly divided into five subsets of equal size, and then each subset is used once to verify the accuracy of the performance analysis model of lithium iron phosphate batte ry based on support vector machine.The model is trained by using the remaining four subsets. The misjudgment rate of four kinds of lithium iron phosphate battery capacity is used as the index of model performance, the average value of five verification results is used as the fitness value of the search agent, and the maximum number of iterations is used as the termination criterion.The iterative process is until the maximum number of iterations is reached, so as to find the global optimal agent containing the optimal model parameters of the support vector machine.

When the parameter optimization process of the WOA-SVM model is completed, the optimal model parameter (C^*, γ^*) with the minimum fitness can be used with the training data set to construct a SVM-based lithium iron phosphate battery performance analysis model. The test data set is used to evaluate the performance of the constructed model.

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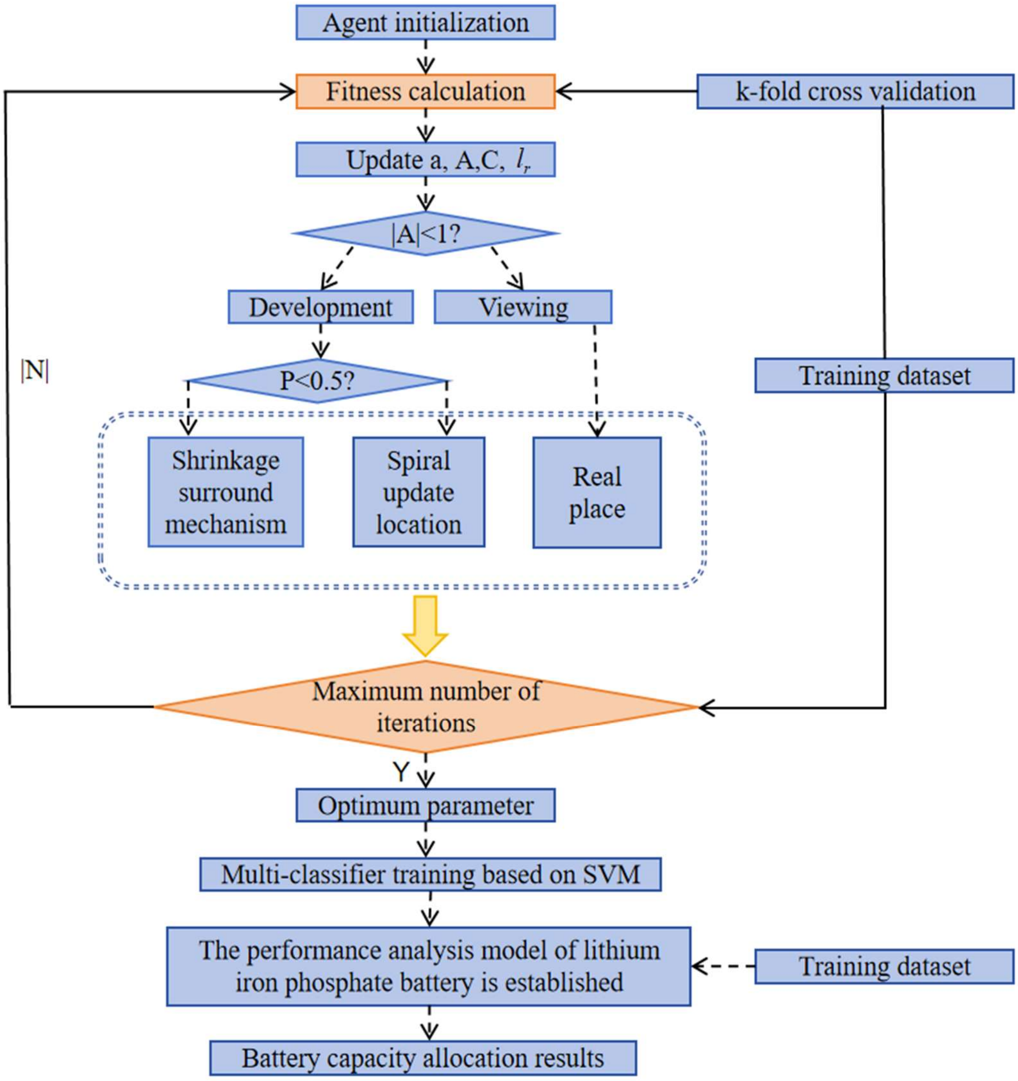

Figure 4. Parameter optimization process of WOA-SVM model

6. Working Principle and Performance Analysis

6.1 Working Principle

Activated alumina is the most studied and widely used adsorbent material for fluoride removal in the world. The adsorption process includes physical adsorption and chemical adsorption.In terms of physical adsorption, activated alumina has a large specific surface area and pore size. The Al_2O_3 raw material used in electrolysis is evenly mixed with the fluorine-containing gas discharged from the electrolytic cell, which can firmly adsorb the fluorine-containing gas.In terms of chemical adsorption, HF adsorption is also fixed by using directional action and induction. The two are different and related to each other, so as to achieve the best efficiency of fluoride removal. The reaction equation is as follows:

$$3Al_2O_3 + 6HF = 3\,[Al_2O_3 \cdot 2HF\,] \tag{1}$$

$$3[Al_2O_3 \cdot 2HF\,] = 2\,AlF_3 + 3H_2O + 2\,Al_2O_3 \tag{2}$$

$$Al_2O_3 + 6HF = 3AlF_3 + 3H_2O \tag{3}$$

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6.2 Reaction Mechanism of Citric Acid

$$6\ H_3Cit\ (aq) + 2LiFePO_4\ (s) + H_2\ A(s) = 2Li^{+}\ (aq) + 2Fe^{2+}\ (aq) + 6H_2Cit^{-}(aq) + 4H_2O + A \quad (4)$$

$$3[Al_2O_3 \cdot 2HF] = 2\ AlF_3 + 3H_2O + 2\ Al_2O_3 \quad (5)$$

$$Al_2O_3 + 6HF = 3AlF_3 + 3H_2O \quad (6)$$

The iron hydroxide precipitate formed by the reaction of ferric iron and carbon dioxide is mixed in the filter slag system, resulting in the purity of the recovered lithium carbonate precipitate is not high, so the use of iron oxide to adsorb an electron of ascorbic acid into ferrous oxide, and finally dissolved by citric acid.A citric acid molecule contains three hydroxyl groups to produce 3mol of hydrogen ions, which not only maintains the concentration of hydrogen ions under strong acid leaching conditions, but also makes the cathode materials dissolve in the system in the form of ions, which is helpful for the next recovery of lithium.

6.3 Performance Analysis

Compared with the traditional inorganic acid recovery system, the leaching of lithium by citric acid-ascorbic acid system not only maintains the reaction environment of strong acid, but also is easier to obtain, reduces the cost, facilitates harmless treatment, avoids the production of chloride, nitrogen oxides and other toxic substances, is more friendly to the environment, and has a certain guarantee in safety.At the same time, compared with HCl or H_2SO_4 used in most processes, citric acid, as an organic ternary acid, can reduce the degree of pH change when adjusting the solution, making the pH adjustment process more stable and controllable, and facilitating the precipitation of different metal ions.

The support vector machine can solve the classification problem in the case of small samples, but for the processing of high latitude and large-scale training samples, the support vector needs to be solved by quadratic programming, which will consume a lot of memory and computing time.In addition, the support vector machine algorithm can only perform two classifications, and the solution to the multi-classification problem is not ideal. Therefore, many intelligent algorithms have been born to optimize SVM parameters so as to achieve the optimal classification of high-dimensional space.However, algorithms such as particle swarm optimization and simulated annealing have the disadvantages of slow convergence speed and easy to fall into local optimum. Therefore, the WOA-SVM method is proposed to optimize the parameters to improve the classification accuracy.

7. Key Technologies and Innovations

7.1 Key Technologies

1) At present, for the recovery of lithium-ion batteries with low capacity, inorganic acid systems are mostly used, which will increase the recovery cost of batteries and produce harmful gases such as HCl and nitrides to pollute the environment. This system uses citric acid-system to recover lithium iron phosphate batteries.The leaching rate of lithium ion in lithium battery by citric acid is more than 95 %, and it is a non-toxic, low-cost and stable organic acid, which has lower requirements for reaction conditions during recovery. In addition, citric acid will also leach the aluminum and iron ions in the system and recover them in the next step.

2) In the process of lithium battery level utilization, WOA optimized support vector machine SVM algorithm is used to classify batteries with different performance.WOA optimization is a meta-heuristic optimization algorithm, which has the advantages of simple mechanism, convenient operation, less parameters and strong optimization ability.This optimization algorithm can greatly reduce the cost consumption and improve the accuracy of matching even if it faces the situation of large amount of data and complex processing process.

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7.2 Innovation

1) In the evaluation of the performance of power batteries with 30 % -80 % capacity, FAHP algorithm is usually used for comprehensive evaluation of models. However, the algorithm is very subjective and there will be artificial errors. Therefore, this system uses entropy weight-TOPSIS method to increase the objective timeliness based on actual data, so that the evaluation results provided are not affected by personal factors, and the weight of specific indicators can also be increased.

2) WOA support vector machine algorithm is used to optimize the hierarchical utilization of lithium iron phosphate battery, which greatly improves its matching speed and ability, and solves the problem of large amount of data. When the number of test sets is more, the training network classification results will be closer to the real value, and the accuracy will be higher.

3) In this system, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester is used to enrich and recover aluminum ions. After processing, it is processed into Al2O3, that is, aluminum electrolytic cell. After adsorbing HF, it is returned to the aluminum electrolytic cell to realize the recovery and utilization of HF, which not only improves the safety factor of the recovery process, but also protects the environment.

4) The system uses citric acid organic acid system to extract lithium from lithium iron phosphate battery. On the premise of improving the leaching rate of lithium ion, it can effectively reduce the cost and protect the environment. In addition, citric acid, as an organic acid, can be recycled and easily degraded, which can also play a guarantee role in the treatment of subsequent waste.

8. Significance of this Project

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8.1 Social Benefits

In 2020, the Department of Energy Conservation and Comprehensive Utilization of the Ministry of Industry and Information Technology promulgated the " Management Measures for the Secondary Utilization of New Energy Vehicle Power Battery " to promote the recycling of waste batteries. The implementation of this plan is in line with the general trend of the development of the times. It is conducive to the establishment of a sound power battery cascade utilization and recycling management system, so that the recycling of waste lithium iron phosphate batteries can get out of the " high input and low return " stage as soon as possible, which greatly promotes the sustainable development of the electric vehicle industry and provides a new perspective for the development of China 's new energy batteries. New solutions inject strong impetus into China 's implementation of a sustainable and economical society.

Power batteries contain nickel, cobalt, manganese, copper, phosphorus, electrolytes and other chemicals that seriously threaten environmental quality and human health. They can be properly handled and recovered. A large number of recyclable high-value metals can increase domestic supply to a certain extent, ensure the safety of China 's resources, and greatly reduce environmental risks. At the same time, recycling power batteries and using recycled materials can effectively reduce carbon emissions and help build a conservation-friendly society.

8.2 Economic Benefits

This technology can be widely used in the recycling of lithium iron phosphate batteries for new energy vehicles. A large part of lithium iron phosphate batteries that meet the scrapping standards can be recycled. By reducing the waste of lithium iron phosphate batteries, the environmental pollution caused by waste lithium iron phosphate batteries is alleviated, and the shortage trend of raw materials for power batteries is slowed down to a certain extent. It can achieve economic benefits, resource conservation and environmental protection ' Trinity '.

With the popularization and application of this technology, the cost of lithium iron phosphate battery will be greatly reduced ; at the same time, not only the new energy automobile industry, but also the lithium iron phosphate battery with the advantages of higher specific energy will be used at a lower cost in various industries, alleviating the economic pressure of power battery manufacturers and promoting the battery market to maintain a strong momentum of sustainable development.

In the process of power battery recycling and pretreatment, the pollution of waste gas, waste liquid and waste residue is reduced, which can prevent the waste power battery from producing more serious secondary pollution. The cost of environmental treatment caused by green treatment of these three wastes will also be reduced accordingly, increasing the number of recycled waste power batteries and further forming a virtuous circle.

8.3 Environmental Benefit

Compared with the traditional inorganic acid recovery system, citric acid, which is environmentally friendly, less corrosive and has strong complexing ability, is used to leach lithium in this paper, which can effectively avoid the generation of toxic substances such as chloride and is more friendly to the environment. At the same time, the chemical waste liquid is recycled and reused, the reaction process is optimized, and the raw materials are used to the greatest extent ; the absorption of hydrogen fluoride in the reaction system reduces its own toxicity, saves limited fluorite resources, and saves energy to a certain extent. It can improve the purity of the product, increase the added value of the product, and protect the environment. It has good economic, social and environmental benefits.

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