

A OUTLINE DISCUSSION ON INFLUENCE OF THE PRECURSOR IRON PHOSPHATE ON THE PERFORMANCE OF LITHIUM IRON PHOSPHATE AND THE OBSERVATIONS OF THE INDUSTRY CHAIN

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ABSTRACT

In this paper, through the preparation of iron phosphate, it is discovered that the quality of iron phosphate product directly affects the electrochemical operation of lithium iron phosphate cathode material. Low dirtiness content and high iron-to-phosphorus relation make lithium iron phosphate electrochemical operation high specific capacity and energy density. in addition to the cost analysis of iron phosphate industry chain, with the capacity gradually saturated, with a phosphate rock resources enterprise as an example, will take and keep by force a great more chances in its industry.

KEYWORDS

Iron phosphate, lithium iron phosphate, electrochemical operation

1. INTRODUCTION

China's power lithium-ion battery industry is expanding quickly due to the popularity and advancement of electric vehicles. Panasonic, LG, and other well-known manufacturers from across the world have invested in building up facilities there and actively developing the power battery market. Domestic battery producers like Ningde Time and BYD are likewise not afraid to make significant investments in increasing their production capacity. Lithium-ion battery materials, notably lithium-iron phosphate, are in short supply due to the booming demand for power lithium-ion batteries as well as the upstream battery material producers. Iron phosphate market, the most significant precursor of lithium iron phosphate materials, is also getting attention.

China's production of iron phosphate increased from 2019 to 2022, notably after 2021, when the country's growth rate in iron phosphate production accelerated. China produced 333,700 tons of iron phosphate in 2017, an increase of 164.72% from the previous year. China will produce 242,000 tons of iron phosphate in the first half of 2022, an increase of 112% from the same time in 2017. China's iron phosphate output has increased dramatically over the last two years, largely as a result of the rise in demand for lithium iron phosphate batteries, which are used in new energy vehicles[1].

The quality of the iron phosphate precursor directly affects the final electrical properties of lithium iron phosphate because the industry's standard production process for lithium iron phosphate first prepares the iron phosphate precursor, followed by the preparation of the lithium source and carbon source. In order to lay the groundwork for the use of lithium iron phosphate as anode materials, it is crucial to develop a robust process synthesis route for iron phosphate. This will not only give technical support for the industrialization of iron phosphate.

2. EXPERIMENTAL SECTION

2.1. Experimental Reagents and Equipment

The main experimental reagents: phosphoric acid (chemical formula H_3PO_4), WPA, industrial grade 85%, a chemical company in Yunnan; ferrous sulfate heptahydrate (chemical formula $FeSO_4 \cdot 7H_2O$), industrial grade I 91.25%, Huixing Chemical Co. Ltd.; hydrogen peroxide (chemical formula H_2O_2), chemically pure 26.8%, Xilong Science Co. Ltd.; Monoammonium phosphate ($NH_4H_2PO_4$), industrial grade 99.5%, a chemical company in Yunnan; Sulfuric acid (H_2SO_4), industrial grade 98%, a chemical company in Yunnan; Lithium carbonate (Li_2CO_3), battery grade, Shandong Ruifu Lithium Industry Co. Ltd.; Polyethylene glycol, analytical purity, Merck Chemical Technology (Shanghai) Co; Aluminum foil (Al), battery grade, Henan Mingtai Aluminum Co., Ltd; Lithium flake (Li), battery grade, Xinghua Benote Battery Materials Co. Ltd.; Polytetrafluoroethylene, battery grade, Atochem, France; N-methylpyrrole (NMP), battery grade, Nanjing Sundaje New Chemical Materials Co. Ltd. Electrolyte ($LiPF_6/EC+DEC$), battery grade, Guangzhou Tianci High-Tech Materials Co., Ltd; Diaphragm, Model Celgard 2400 Polypropylene, Beijing Xingya Shenyuan Science and Trade Co Ltd; Acetylene Black, Battery Grade, Tianjin Huayuan Chemical Technology Co Ltd etc and other common reagents.

Table 1. Product indicators of ferrous sulfate heptahydrate

Indicator items	Indicators	
	I	II
Mass fraction of ferrous sulphate ($FeSO_4 \cdot 7H_2O$)/% \geq	90.0	90.0
Mass fraction of titanium dioxide (TiO_2)/% \leq	0.75	1.00
Mass fraction of substances insoluble in water/% \leq	0.50	1.00
Mass fraction of free acid (as H_2SO_4)/% \leq	1.00	-
Mass fraction of arsenic (As)/% \leq	0.0001	-
Mass fraction of lead (Pb)/% \leq	0.0005	-

Main experimental instruments and equipment: glass reactor, size 2L, Asahi, Japan; constant temperature water bath, model RC-HH-4, Beijing Ruicheng Yongchuang Technology Co. Ltd.; Stirrer, model Eurostar 20, IKA Group, Germany; Electrothermal Constant Temperature Drying Box, model DHG-9245, Shanghai Hengyi Technology Co. Ltd.; Plate and frame filter press, model SHXB, Shanghai Xinbu Technology Co.Ltd.; Precision electronic balance, model JJ100, Jiangsu Changshu Shuangjie Testing Instrument Factory; High temperature tube atmosphere furnace, model LYL-18DG, Luoyang Liyu Furnace Co.Ltd.; Lithium battery glove box, model Smart series, Aimingke Technology (Beijing) Co Ltd; battery test system, Series 4000 high precision battery test equipment, Shenzhen Xinrui New Energy Technology Co Ltd; Makan mortar and other common utensils.

2.2. Iron Phosphate Product Analysis, Apparent Properties Testing

Specific surface area, particle size and size distribution, compaction density, iron-phosphorus ratio, water content, and impurity content are some of the indications of iron phosphate products.

The method and pertinent requirements of HG/T 4701-2014 "Iron phosphate for batteries"^[2] are used to analyze and test the contents of each chemical composition of ferric phosphate; the applicable requirements of GB/T 5162 "Determination of vibrational density"; impurity elements are analyzed and tested according to the relevant requirements of GB/T 3902-2014 "Determination of impurity elements in inorganic chemical products ICP-OES"; particle size distribution of ferric phosphate products is tested by Malvern particle size analyzer.

2.3. Lithium Iron Phosphate Button Cell Assembly and Preparation of the Precursor Iron Phosphate

In this experiment, ferrous sulphate, monoammonium phosphate and hydrogen peroxide were used as raw materials to synthesise ferric phosphate dihydrate in certain proportions and under suitable process conditions. The reaction's product, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, was placed in a vessel and roasted in a muffle furnace at a suitable temperature for a certain period of time to produce light yellow anhydrous FePO_4 .

Additionally, both domestically and internationally^[3], the methods for synthesizing lithium iron phosphate can be broadly classified as either solid phase methods or liquid phase methods. Auxiliary components including hydrogen peroxide, glucose, ammonia, sodium hydroxide, carbon black, etc. are required. This experiment was prepared by mixing anhydrous ferric phosphate with lithium source (e.g. battery grade lithium carbonate), organic carbon source (e.g. glucose, polydiethanol, etc.) in a certain ratio, molar ratio $\text{Li:Fe:P}=1:1:1$ and adding appropriate amount of anhydrous ethanol as solvent in a ball mill for 18-20 hours to make a good mixture. It was then removed, dried, crushed, and put into a tube furnace with inert gas protection (e.g. nitrogen) and roasted at a constant temperature of $720 \pm 20^\circ\text{C}$ for 8-10 h to finally produce LiFePO_4 cathode material. The following is the reaction equation for the preparation of lithium iron phosphate.



Lithium iron phosphate button cell assembly^[4]: LiFePO_4 powder, acetylene black and polytetrafluoroethylene were mixed thoroughly in a certain ratio, made into a slurry with a solution of battery-grade N-methylpyrrole NMP, evenly coated on aluminium foil, vacuum dried, rolled and then punched into a circular electrode sheet of specified area. A lithium metal sheet was used as the negative electrode, a Celgard 2400 polypropylene film as the diaphragm and a 1 mol/L EC+DEC (1:1 molar ratio) solution of LiPF_6 as the electrolyte, which was assembled into a button cell in a glove box filled with argon gas. Stand for 12 hours at 25°C the buckle batteries were tested by the Series 4000 high precision battery test equipment for constant current charge/discharge cycles.

3. RESULTS AND DISCUSSION

3.1. Comparison of Prepared Iron Phosphate Product Indicators with Industry Indicators

The raw materials for the experimental preparation process are ferrous sulphate, monoammonium phosphate, and hydrogen peroxide. Under the right conditions, a specific ratio of ferric phosphate dihydrate is obtained, and it is then further roasted at a high temperature to produce anhydrous ferric phosphate. The product index of ferric phosphate dihydrate and ferric phosphate for batteries should be in accordance with HG/T 4701-2014 technical index shown in Table 2.

Table 2. Product indicators and technical specifications of ferric phosphate dehydrate

Items		Sample 1	Sample 2	Sample 3	Sample 4	Standard indicators
P, w%		17.0	17.1	17.0	17.1	16.2-17.2
Iron-phosphorus ratio		0.98	0.99	0.98	0.99	0.97-1.02
Ca , w/%	≤	0.001	0.001	0.001	0.001	≤0.005
Mg , w/%	≤	0.001	0.001	0.001	0.001	≤0.005
Na , w/%	≤	0.005	0.005	0.005	0.005	≤0.01
K , w/%		0.005	0.005	0.005	0.005	≤0.01
Cu , w/%		-	-	-	-	≤0.005
Zn , w/%		0.001	0.001	0.001	0.001	≤0.005
Ni , w%		-	-	-	-	≤0.005
Sulphate (as SO ₄ ²⁻), w/%	≤	0.005	0.005	0.005	0.005	≤0.01
Chloride (as Cl ⁻), w/%		-	-	-	-	≤0.01
Moisture, W/%		19.5	19.8	20.2	20.0	19.0-21.0
Vibrational density, (g/cm ³)		0.73	0.71	0.70	0.72	≥0.7
Grain size (D ₅₀) , μm		5.45	5.15	4.86	4.24	2-6

As can be seen from the data in Table 2, all the indicators of the four groups of products prepared by the process are in line with and better than the industry standard battery-grade iron phosphate HG/T 4701-2014, and also meet the requirements for the preparation of battery-grade lithium iron phosphate cathode materials.

3.2. Lithium Iron Phosphate Electrochemical Performance Testing

Under the other processes remain unchanged, different Fe/P iron phosphates were taken to synthesize lithium iron phosphate and assembled into button cells in a special glove box for lithium batteries and tested for electrochemical performance. Table 3 displays the test's experimental outcomes.

Table 3. Test results on the lithium iron phosphate's electrochemical performance at various main element ratios

Samples	Proportion of main elements in lithium iron phosphate			First charge ratio capacity (mAh/g)	First discharge ratio capacity (mAh/g)	First cycle efficiency (%)	10 times discharge ratio capacity (mAh/g)
	Li	Fe	P				
Sample 1	1.03	0.98	1	155	140	92	141
Sample 2	1.04	0.97	1	153	138	91	140
Sample 3	1.03	0.96	1	152	137	91	140
Sample 4	1.03	0.96	1	150	136	93	140
Comparison 1	1.03	0.90	1	130	115	88	82
Comparison 2	1.04	0.91	1	127	117	92	83
Comparison 3	1.03	0.87	1	135	125	93	98
Comparison 4	1.03	0.90	1	140	126	90	85

The data in Table 3 demonstrate how even small variations in the proportions of various elements can result in significant variations in material performance, product consistency, stability is a difficult point, we believe that there are differences between different companies iron phosphate products. Take the iron-phosphorus ratio as an example, when the iron-phosphorus ratio reaches 0.96-0.98, the first charge specific capacity can be as high as 155 mAh/g, the first discharge specific capacity can be as high as 140 mAh/g, the first cycle efficiency is 93%, 10 times the discharge specific capacity can be as high as 141 mAh/g. The first cycle efficiency is 88%, the first charge specific capacity is 127 mAh/g, the first discharge specific capacity is 117 mAh/g, and the 10 times discharge specific capacity is roughly 83 mAh/g while the iron-phosphorus ratio is smaller than 0.91.

Therefore, to increase the specific capacity of iron phosphate batteries and their material cycle life^[5], you can control the iron phosphate product indicators through the synthesis process, such as low impurities, high iron-phosphorus ratio, high crystallinity of iron phosphate, and synthetic lithium iron phosphate. The battery's material cycle life was greatly improved when the specific capacity and energy density were applied; nevertheless, the battery's low temperature performance was poor due to the presence of impurity ions, which produced lattice distortion and blocked the lithium ion diffusion channel.

The shape of the iron phosphate particle has a sizable impact on the electrochemical performance of lithium iron phosphate batteries. We found that the spherical shape of iron phosphate is conducive to reducing the internal resistance of lithium iron phosphate batteries, making the diffusion impedance of lithium ions lower, thus making the multiplicative performance of lithium iron phosphate batteries significantly improved; additionally, the iron phosphate's spherical shape has a higher stacking density, better flow, and better dispersion, which is helpful in producing cathode material slurry and electrode coating, improving the performance of the electrode sheet, thus improving the electrochemical performance of the battery.

4. COST ANALYSIS OF THE IRON PHOSPHATE INDUSTRY CHAIN

In this experiment, the raw materials for the production of ferric phosphate are ferrous sulphate, monoammonium phosphate, and hydrogen peroxide. Monoammonium phosphate is primarily made from phosphate ore, sulfur, and ammonia as basic ingredients. Monoammonium phosphate is created by combining artificial ammonia (made from coal and natural gas) with wet phosphoric acid, which is created from phosphate ore and sulfur. Figure 1 depicts the process of ferric phosphate production.

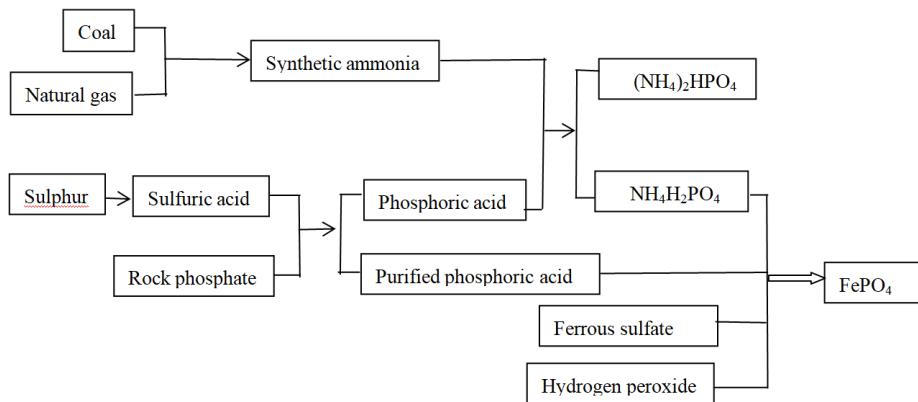


Figure 1. Iron phosphate synthesis process route

For the production of 1 t of monoammonium phosphate, which is assumed to be produced externally, 1.9 t of phosphate rock, 0.45 t of sulphur, and 0.13 t of ammonia are needed. Phosphate rock, sulfur, and ammonia make up 44.5%, 42.1%, and 13.4%, respectively, of the cost of monoammonium phosphate's raw materials. The raw material cost of monoammonium phosphate is shown in Table 4.

Table 4. Raw material cost budget for monoammonium phosphate

Raw material	Consumption per ton (ton)	Price (CNY/ ton)	Cost (CNY/ton)	Cost ratio (%)
Rock phosphate	1.9	1000	1900	44.5
Sulphur	0.45	4000	1800	42.1
Synthetic ammonia	0.13	4400	572	13.4
Total (CNY/ ton)			4272	

If monoammonium phosphate costs are further broken down, a company with phosphate resources, for example, in 2021, the costs of raw materials, freight, manufacturing costs, direct labor, and fuel and power accounted for roughly 72%, 13%, 7.6%, 2.1%, and 5.3% of total costs, respectively. The monoammonium phosphate segment is still mostly made up of raw materials.

The price of the raw ingredients needed to synthesize the ferric phosphate for this experiment was then broken down according to market rates. The production of 1 tonne of ferric phosphate requires the consumption of approximately 0.78 tonnes of industrial grade monoammonium phosphate, 0.1 tonnes of phosphoric acid (85%), 2.05 tonnes of ferrous sulphate, 0.55 tonnes of hydrogen peroxide, 0.13 tonnes of sulphuric acid (98%) and other costs including labour,

manufacturing, fuel, transport etc. accounting for 37% of the total costs. The largest proportion of the raw material side of the cost of industrial grade monoammonium phosphate and ferrous sulphate accounted for 38.6% and 9.1% respectively, in addition to phosphoric acid (85%) cost accounted for 8.9%, hydrogen peroxide cost accounted for 5.6% and sulphuric acid (98%) cost accounted for 0.8%. Among them, monoammonium phosphate and phosphoric acid can come from phosphate fertilizer enterprises, ferrous sulfate from titanium dioxide enterprises by-product. The cost of producing 1 tonne of ferric phosphate is shown in Table 5.

Table 5. Budget for iron phosphate production costs

Raw material	Consumption per ton (ton)	Price (CNY/ ton)	Cost (CNY/ton)	Cost ratio (%)
Monoammonium phosphate	0.78	5800	4524	38.6
Phosphoric acid (85%)	0.1	10500	1050	8.9
Ferrous sulfate	2.05	520	1066	9.1
Hydrogen peroxide	0.55	1200	660	5.6
Sulfuric acid (98%)	0.13	700	91	0.8
Other cost			4340	37.0
Total (CNY / ton)			11731	

According to Table 5, the price to produce one ton of ferric phosphate ranges between 11500 and 13000 yuan . The total cost of ferric phosphate produced using this method can be kept under control at 12000-14000 yuan, giving the ferric phosphate industry a significant competitive market advantage. One ton of ferric phosphate by-products equals roughly one ton of ammonium sulphate, and ammonium sulphate is currently priced at about 1400–1600 yuan/tonne. For ferric phosphate enterprises with phosphate ore resources, profitability will be significantly improved. Currently the price of ferric phosphate with tax is 23000 yuan/tonne.

5. CONCLUSIONS AND OUTLOOK

Lithium iron phosphate cathode material performance is directly influenced by the quality of the precursor iron phosphate product; by controlling the granular form of the precursor, combined with low impurity content and high iron to phosphorus ratio, the specific capacity of lithium iron phosphate products is increased, cycle life is extended and low temperature performance is improved.

Additionally, in the context of global carbon neutrality, electrification is an inevitable trend. According to incomplete statistics, CO₂ emissions have grown at a compound rate of approximately 2.0% from 1965 to 2019, 1.9% from 2000-2019 and 1.1% from 2010-2019. The growth rate is declining as a whole. Among them, transportation accounts for 25% of all worldwide carbon emissions, making it the primary source of these emissions. Because of the need for a higher percentage of electricity in end-use energy consumption to achieve carbon neutrality standards, the amount of electricity used in the transportation industry will multiply between 10 and 40 times between 2030 and 2050.

According to available data, 1GWh of lithium iron phosphate requires about 0.23-0.27 million tons of cathode material, we take 0.25 million tons as the base for calculation. This corresponds to 0.182 million tonnes of industrial grade phosphoric acid or 0.182 million tonnes of monoammonium. With 315GWh in 2025 and 960GWh in 2030, lithium iron phosphate material is about 780,000 tonnes and 2.4 million tonnes, corresponding to 930,000 tonnes and 2.88 million tonnes of raw material ferric phosphate dihydrate, corresponding to about 600,000 tonnes and 1.75 million tonnes of phosphoric acid. Companies that produce phosphorus chemicals, for instance, have their own stable manufacturing lines, and the benefits of integration with the precursor iron phosphate business will make the company more competitive.

As the nation develops its new energy sector, demand for new phosphorus-based materials such as ferric phosphate will rise significantly in the future. Many phosphorus chemical companies currently have new phosphorus-based materials capacity plans and continue to expand into new energy areas, giving traditional phosphorus chemical companies a new lease of life.

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