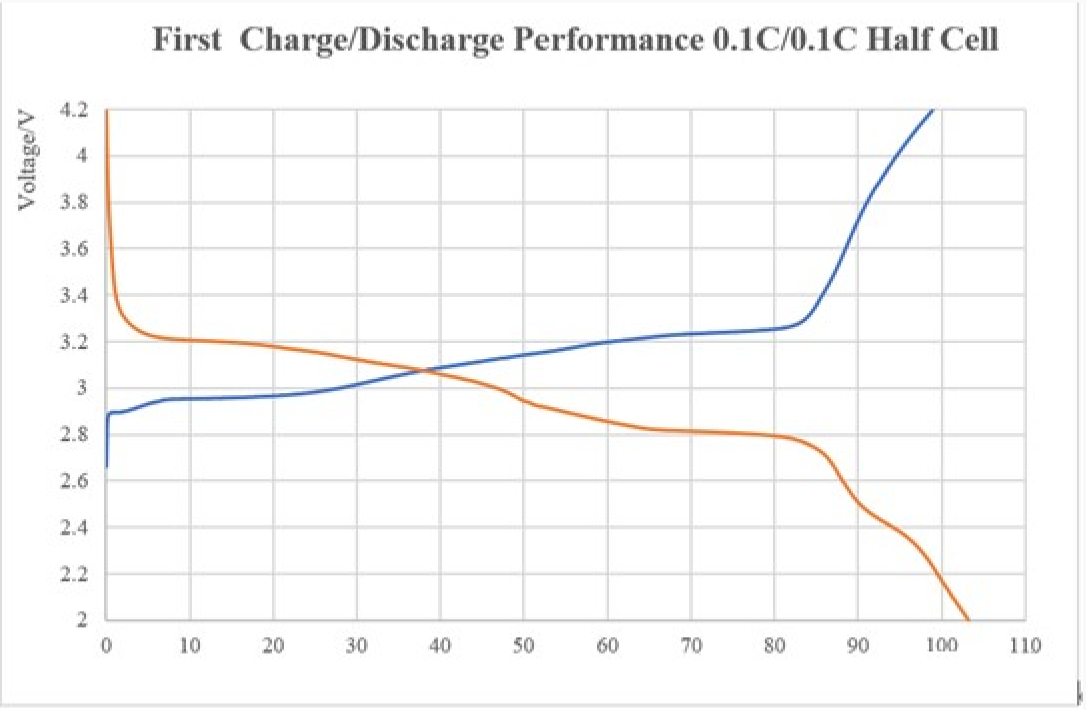
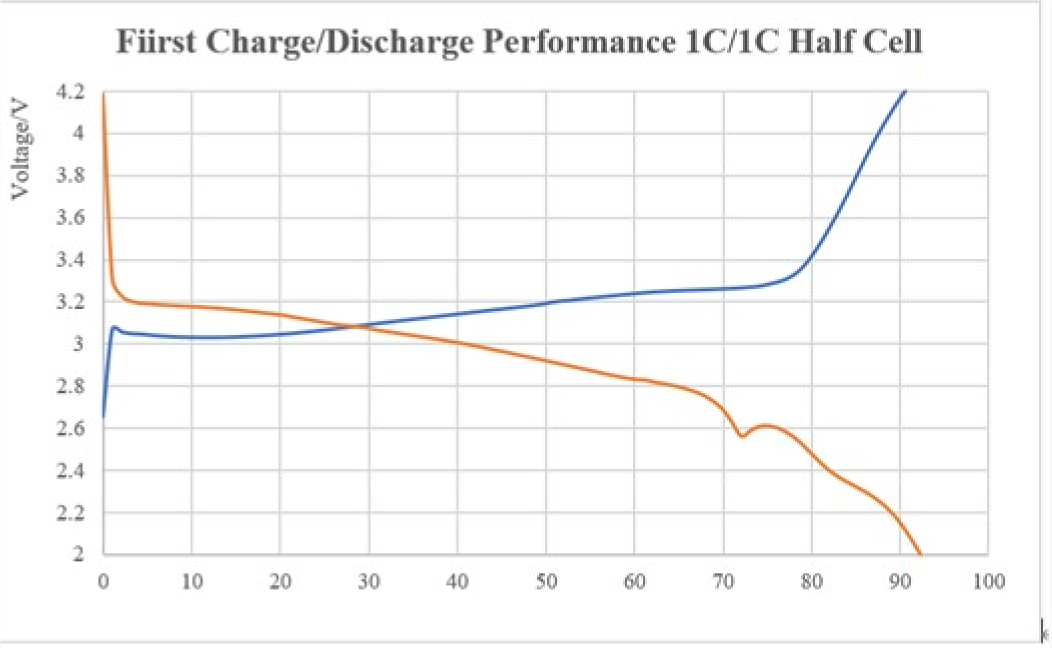
A brief introduction to the internet celebrity sodium electrode cathode material: sodium ferric pyrophosphate NFPP

The full name of NFPP is sodium ferric pyrophosphate (Na4Fe3P2O7(PO4)2 and its derivatives). Taking the most mainstream Na4Fe3P2O7(PO4)2 as an example, the theoretical gram capacity is 129mAh/g, and the actual gram capacity is 105mAh/g (0.1C Dis.) and 95mAh/g (1C Dis), and the actual gram capacity is still a charge-off data. The positive electrode is coated very thin, and the negative electrode is made of sodium metal sheet; if it is made into a full battery, the negative electrode must be made of hard carbon, and the gram capacity Another 10% off. The tap density is 0.8g/cm3, the compaction density is generally around 1.9g/cm3, the rated operating voltage is around 3.0V (0.2C Dis.), and in terms of cycle life, 100% DOD 2.0-4.0V Cycle>4000 is not a big problem.





Let's start with a few questions:

1. Why choose NFPP instead of other polyanionic compounds?

Let's first talk about why sodium iron phosphate ($NaFePO_4$) is not used. Many people may think that lithium iron phosphate can be replaced by simply replacing Li with Na. However, currently, olivine sodium iron phosphate cannot be directly chemically synthesized. The most commonly used simple preparation method is the ion exchange method based on organic solutions (ion exchange method), which is divided into two steps. The first step is to remove lithium from lithium iron phosphate to obtain iron phosphate. The second step is to charge the iron phosphate obtained after delithiation with sodium to obtain sodium iron phosphate. However, the electrochemical performance of sodium iron phosphate obtained by this method is not ideal. Its capacity is usually 100-120mAh g-1, and obvious capacity fading will occur after 100 cycles.

In a word, sodium iron phosphate synthesized by direct sintering has no electrochemical activity. If you have to make active sodium iron phosphate, you have to use ion exchange method. Even so, the performance is very poor;

What about sodium ferric pyrophosphate? Yes, sodium iron pyrophosphate ($Na_2FeP_2O_7$) can be used and has a three-dimensional sodium ion channel, but when you look at the large molecular weight, you know that the theoretical gram capacity is too low, shockingly low; and the material is extremely unstable and is very toxic in the air. Easily denatured by oxidation;

Someone must ask, what about the sodium iron sulfate $Na_2Fe_2(SO_4)_3$? Of course, there are definitely many advantages, but there are also quite a few disadvantages, even fatal. Let me just say one thing: How to remove crystal water during the manufacturing process is a lot of work and effort. The laboratory is okay, but extreme measures are not required. What about after the pilot test? What about after mass production? How can we ensure that crystal water is completely removed and how can we ensure batch consistency? In terms of cycle performance, the S element is a variable element, and SO_4 has a valence of +6, so the oxidation property is not low, which will inevitably lead to poor cycle performance; the rate performance is also criticized, and the sodium ion transmission path and resistance are also problems;

Others, such as V-based F-based Mn-based polyanion compounds, have their own problems that are more or less difficult to commercialize and will not be discussed again.

	Prussian Series	Phosphate Series	Layered Oxide Series
Material	Sodium Ferrocyanide modification	Sodium vanadium phosphate, Sodium vanadium fluorophosphate, Sodium ferric pyrophosphate, sodium ferric sulfate	Sodium copper ferromanganate, Sodium nickel ferromanganate
Working Voltage	3.1~3.4V	3.1~3.7V	2.8~3.3V
Discharge specific capacity	70-160mAh/g	100-110mAh/g	100-140mAh/g
Compacted	1.3-1.6	1.8-2.4	3.0-3.4

density			
Cycle life	Fair	Better	Fair
Thermal Stability	Better	Fair	Fair
Safety	Low	Low	Good
Air Stability	Good	Better	Fair
Corresponding battery weight and volumetric energy density	Low	Low	Better

2. Future R&D development direction of NFPP:

Let's talk about the most mainstream and reliable direction: different measurement ratios of each element. The current mainstream NFPP material is Na4Fe3P2O7(PO4)2, because the material synthesis under this stoichiometric ratio is the simplest, has relatively few miscellaneous items, the most stable structure, and the best safety; but the biggest problem is that the actual theoretical capacity is low. In the future, various metering ratios need to be adjusted to increase the gram capacity, which of course may sacrifice some other performance.

Another one is the D50 direction: the Na+ solid phase diffusion transmission rate of NFPP is too low. In order to ensure that the electrochemical performance can be effectively exerted, the primary particles and secondary particles cannot be made too large. However, if the D50 is too small, it will affect the new material processing capabilities and Compaction density, etc., will also increase the reaction interface between the surface of the cathode material and the electrolyte, and increase side reactions; then how to make the particle size the most suitable size and take into account all aspects of performance is a difficult problem;

The other one is doping, doping with different metal elements (Mg Ti, etc.) to improve stability, gram capacity, safety performance, etc.

Test Item			Unit	Standard Value	Typical Value	Test Method
Physical indicator	Particle size distribution	D10	μm	≥0.5	0.52	GB/T 19077.1
		D50		3.0±0.3	3.1	
		D90		≤9.0	7.80	
	Specific surface area		㎡/g	15±3	16.8	GB/T 13390
	Tap density		g/cm³	0.8±0.05	0.82	GB/T 5162
	Compacted density		g/cm³	1.95±0.1	1.95	Compaction density meter
	Moisture		ppm	≤800	730	Calfi Moisture Meter
	PH		/	10±0.5	10.2	PH meter

3. NFPP cost price:

The price of NFPP is also one of the biggest advantages. Compared with the current layered oxides, the raw material price of one ton of sodium nickel ferromanganate (NaNiFeMnO 1/3 1/3 1/3) is about 35,000; while the raw material price of one ton of NFPP is between 11,000 and 13,000 (price The range is mainly due to different iron sources). Moreover, the sintering temperature of layered oxides is generally high, generally close to 900°C, while that of NFPP is less than 600°C. Regarding industrial manufacturing costs, the price of NFPP is lower;

Due to the current imperfection of the sodium-ion battery industry chain, high raw material prices and low market demand lead to low production capacity and high production costs; the final actual selling price will definitely be much higher, but taking into account market acceptance and competitiveness, there may even be Due to pressure from investors, in fact, all material manufacturers are selling at low prices and losing money; for example, the market price of a company's layered oxide material sodium nickel ferromanganate (NaNiFeMnO 1/3 1/3 1/3) is 4.5w/ton, single BOM The cost, not including industrial production losses, reaches 3.5W/ton, which is evident;

How much will NFPP sell for in the future? Give you a data reference. If calculated based on 8% net profit, if the NFPP production capacity reaches 2,000 tons/year, the NFPP selling price should be around 3W/ton; if the production capacity reaches 10,000 tons/year, the NFPP selling price should be around 2.5W/ton, reaching 50,000 tons/year , the selling price of NFPP should be close to around 2.2W/ton.

You have to ask, what is the current price of NFPP? All I can say is that the price doesn't make any sense now. Our production capacity has not been increased, and the manufacturing costs (mainly electricity costs) are there.

4. Where is NFPP used?

You can completely understand NFPP as lithium iron phosphate currently on the market. The advantages of NFPP and lithium iron phosphate are almost the same, including cheap price, long cycle life, high safety, and no environmental pollution; the disadvantages are also the same, such as low energy density and low temperature. Poor performance and poor rate performance;

Therefore, the best application scenario of NFPP is energy storage, such as small storage, household storage, outdoor base station energy storage, photovoltaic energy storage, etc. Of course, some low-speed vehicles and two-wheelers that do not have high mileage requirements are also suitable; at the same time, some Scenarios with higher safety requirements, such as airport sweepers, are also a good choice;

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