PFAS Restriction Feedback (PVDF & PTFE)

1. Background

Carbon peaking and carbon neutrality goals:

The European Commission aims to reduce net greenhouse gas emissions by at least 55 percent by 2030 compared with 1990 levels, and to achieve "carbon neutrality" by 2050, which means reducing net carbon emissions to zero. Achieving "carbon neutrality" requires joint action in seven strategic areas, including improving energy efficiency; developing renewable energy; developing clean, safe and connected transport; developing competitive industries and circular economies; promoting infrastructure and connectivity; developing bioeconomies and natural carbon sinks; and developing carbon capture and storage technologies to address remaining emissions. The transport sector is one of the most important emission reduction objects, in order to cope with climate change, and to achieve the goal of carbon neutrality in 2050, the EU plans to 2030, the newly registered fuel vehicles will be 55% less than in 2021, By 2035, the European Union will ban the sale of new fuel vehicles with non-zero carbon emissions. This will accelerate the development of the new energy vehicle industry in Europe. Traditional European car companies have accelerated the "electrification" transformation, and the sales scale of new energy vehicles in Europe has expanded rapidly. According to data released by the European Automobile Manufacturers

Association (ACEA), in June 2023, the number of pure electric vehicle registrations in Europe was about 210,000, a 55% increase year-on-year. From January to June 2023, the cumulative registrations of pure electric vehicles in Europe rose by 45% year-on-year to 930,000. Europe has become one of the world's major consumer markets for new energy electric vehicles and has maintained a rapid development momentum. With the outbreak of the European new energy vehicle market, the European power battery market demand will increase significantly. Under the current European vehicle CO_2 emission policy, European power battery production has grown from around 50 GWh in 2020 to close to 120 GWh in 2022, and is expected to exceed 300 GWh by 2025, with a compound annual growth rate of more than 40% from 2020 to 2025. The industrial development of new energy is of great significance for the EU to achieve sustainable development and carbon neutrality goals.

The issuance of restrictions on perfluorinated and polyfluoroalkyl substances (PFAS) will create a huge obstacle to the new energy battery industry. Because, so far, in the power battery industry, (1) the positive electrode of the battery preparation process is almost all PVDF binder, and there is no binder in the short term to fully replace PVDF without affecting the battery performance; (2) The PTFE binder used in the dry electrode process cannot be replaced due to the appropriate fibrosis processing technology.

2. Irreplaceability analysis of PVDF binders

In addition to the adhesive characteristic of the general binder, the lithium-ion battery binder also needs to be able to withstand the swelling and corrosion of the electrolyte, as well as withstand the electrochemical corrosion during the charge and discharge process, and maintain stability within the working voltage range of the electrode, so there are not many polymer materials that can be used as the lithium-ion battery electrode binder.

2.1 PVDF oil-based binder

PVDF is a highly non-reactive thermoplastic fluoropolymer, the most important in lithium batteries is used as a positive binder and diaphragm coating material, although the positive binder in the positive mass is usually only 1% to 3%, but it is the main source of the mechanical properties of the entire electrode, the electrode production process and the electrochemical performance of the battery has an important impact. PVDF, as the most commonly used positive binder, has a permeability of more than 90%. PVDF has many advantages: it has a wide electrochemical stability window and stable electrochemical performance at 0-5V (Li/Li^+); It has good antioxidant capacity and chemical inertness and is not easy to deteriorate. The electrode electrolyte with PVDF as binder has good swelling property and better wettability. Therefore, PVDF binder is the first to be commercialized because of its wide source and excellent performance, and the battery preparation process using PVDF as binder has also been established.

Although, with the development of new energy, the shortcomings of PVDF binders have gradually become prominent. PVDF is a semi-crystalline polymer, although it has excellent electrochemical and chemical stability, but its own electronic and ionic conductivity is weak. At the same time, the bonding effect of PVDF binders generally comes from the intermolecular van der Waals force and the hydrogen bond formed by the C-F bond on the main chain and other substances in the electrode. In addition, the molecular weight of PVDF decreases after water absorption, and , and the cohesiveness became worse, so the humidity requirements of the environment are relatively high; PVDF needs to use N-methylpyrrolidone (NMP) as a solvent, which has a high volatile temperature and needs to be equipped with a corresponding solvent recovery system. Young's modulus is relatively high, between 1-4 Gpa, and the flexibility of the pole sheet is not good enough. To this end, researchers have improved the PVDF structure from various angles in recent years, mainly including grafting, blending and copolymerization, in order to obtain better performance and ensure that it is more suitable for use in lithium batteries. The graft modification of PVDF binder generally takes PVDF as the main body, and small molecules or inorganic particles are dispersed in PVDF, often there will be chemical bonds between them. In the modification of PVDF binder, blending modification is simple and effective, generally by mixing another polymer with PVDF to obtain a better binder. Common polymers blended with PVDF are polyethylene glycol (PEG), polymethyl methacrylate (PMMA) and polyvinyl acetate (PVAC). After blending, the modified binder generally shows that the PVDF crystallization is decreased, the composite electrode is more friendly to the electrolyte, the lithium ion transmission is accelerated, and the battery performance is improved.

PVDF is also often copolymerized with fluorine-containing molecular segments, such as hexafluoropropylene, tetrafluoroethylene, etc., to obtain functional binders. The researchers used PVDF-HFP (polyvinyl chloride hexafluoropropylene) as a heat sensitive binder (TSB) [1] and cross-linked it, and found that TSB can effectively reduce the peak temperature of the internal short circuit without affecting the cyclic performance of LIB, which has a significant effect on alleviating the thermal runaway of lithium-ion batteries.

However, such modifications still have polyfluoroalkane structures such as $-CF_2-$ and $-CF_3-$.

2.2 Non-PVDF oil-based binder

In addition, scientists are also developing other non-PVDF oily binders, mainly including: polyacrylonitrile (PAN), polyimide (PI), perfluorosulfonic acid ionomers (Nafion).

PAN is a semi-crystalline polymer with a strong polarity of the nitrile group as its main functional group, generally connecting active substances and current collector through hydrogen bonding, van der Waals forces, and permanent dipole-dipole interactions. At the same time, PAN can infiltrate the electrolyte well, and the strong polarity of nitrile can also promote the movement of lithium ions in the electrode.

PI binders generally have good mechanical properties and heat resistance, and they are often used in large volume expansion of silicon negative electrode and high pressure layer positive electrode materials.

Nafion has excellent ionic conductivity and suitable bond strength. The sulfonic acid group on Nafion can produce electrostatic interaction with Li^+ in the electrolyte, and make Li^+ creep and migrate on the polymer main chain to improve the ionic conductivity of the electrode. Although the use of non-PVDF oil-based binders in the positive electrode has certain potential, there are still some problems that limit its application. Professor Daniel Brandell et al [2，3]. of Uppsala University in Sweden used polyacrylitrile as a binder. Due to the degradation and parasitic reaction of PAN, the internal resistance of the electrode in the cycle increased. Polynitriles should be used with caution in high-voltage batteries. Compared with pure PVDF, PI causes greater polarization [4]. In addition, when PI binder is used alone to replace PVDF, its processing performance is poor due to its rigid structure, and the problem of its flexibility needs to be further solved.

Although the scientific community and the business community are looking for a more suitable oil-based binder, PVDF still has significant advantages compared with other materials in high voltage resistance, adhesion, stability, and conductivity, in the field of positive electrode binder materials, it is difficult to appear substitutes that can directly replace PVDF binder materials in the short term. In addition, in the field of power batteries, the iteration of new materials requires longer production feasibility verification, electrical performance verification, and safety verification in order to bring products to market. According to ITAF16949 quality system, if the material of existing products is changed, it needs to be re-verified from the A sample.

In summary, in the field of positive electrode binder materials, we hereby apply for an exemption from the restrictions on the application of PVDF in the positive electrode of the battery.

3. Irreplaceability analysis of PTFE binders

3.1 The significance of dry electrode

The traditional wet electrode preparation uses water solvent or N-methylpyrrolidone solvent, so its thermal drying process is extremely time-consuming and energy consuming. In addition, due to the toxicity of N-methylpyrrolidone, expensive recycling equipment must be invested to solve the environmental problem, which amplifies the time and energy costs. In view of this, the scientific community and industry have been committed to developing solvent-free dry preparation technology for lithium electrodes to achieve green battery production.

Compared with the existing wet electrode manufacturing technology, the dry electrode technology will have a disruptive impact on the entire lithium battery industry [5].

(1) Reduce energy consumption

First of all, due to the change of the process, the wet slurry allocation, coating, drying process is completely eliminated, the length of the production line can be reduced by about 70%, the equipment investment cost is reduced by 20%, and the energy consumption is reduced by 50%, which meets the requirements of "low carbon and energy saving".

(2) Increase energy density

The EU's "Battery 2030+" pointed out that: to create high-performance batteries, the battery actual performance (energy density and power density) and theoretical performance of the gap between at least 1/2, the industry generally plans to 2025 power battery specific energy reached 400 Wh kg^{-1}, 2030 energy density reached 500 Wh kg^{-1}. Therefore, high energy density is the long-term development direction of power batteries.

According to the Maxwell report, the current energy density of dry electrode batteries has reached more than 300 Wh kg^{-1}, which is more than 10% upgrade than ordinary products, and in 2025, it will reach more than 350Wh kg^{-1}, and the cost per kwh will be reduced to less than \$100, and after 2025, it will achieve > 500 Wh kg^{-1}.

(3) Green environmental protection

Dry electrodes do not use solvents such as NMP, which is more environmentally friendly.

3.2 Irreplaceability of PTFE material in dry electrode process

During the preparation of the dry electrode, the adhesive polymer material needs to be formed into a fibrotic network by shear force, and then conductive carbon and the active substance are closely combined to form an unsupported electrode, and then the unsupported electrode is rolled onto the current collector by hot pressing. The SEM is shown in Figure 1.

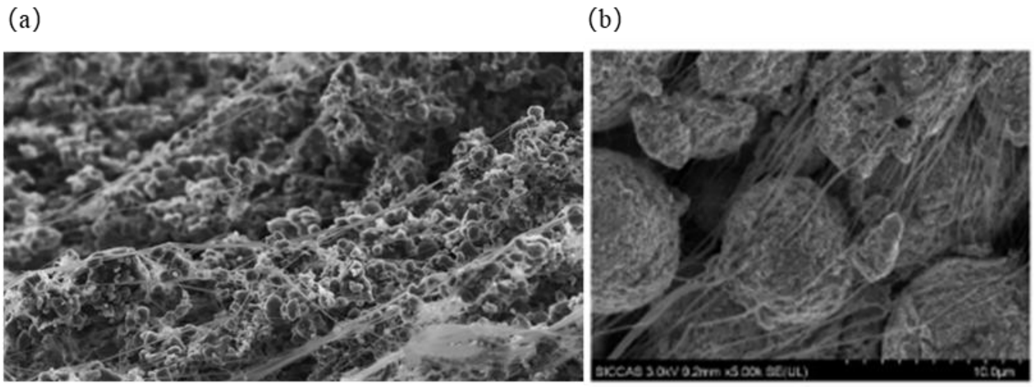

Figure 1. SEM of dry electrode (a) dry electrode of LFP (b) dry electrode of NCM

Polytetrafluoroethylene (PTFE), its chemical structure formula -(CF_2)n-, the relative molecular mass from one hundred thousand to ten million. PTFE has a special crystal fault, and the polymer structure has limitations on the choice of slip plane. Therefore, when a shear load is applied to the PTFE crystal, crystal slip occurs along the C-axis, and the shape of the PTFE crystal changes, enabling the formation of a nanofiber structure with a high length-to-diameter ratio.

Commonly used fibrosis binder include PTFE [6], ETEF (ethylene-tetrafluoroethylene copolymer) [7] and FEP (tetrafluoroethylene hexafluoropropylene copolymer), which are fluorinated substances, PVDF cannot be fibrillated, but it can still be used to spray PVDF and other active particles onto the current collector, and the mixture is rolled after heat treatment. However, the adhesion effect was poor, and the adhesion strength of PVDF was less than 1/4 of that of FEP. The reason is that the particle size of PVDF is too large, which weakens the adhesion effect and reduces the stability of the electrode film. ETEF (ethylene-tetrafluoroethylene copolymer) due to the introduction of vinyl monomer, the ethylene/tetrafluoroethylene ratio in the copolymer is close to 1/1, its heat resistance temperature is lower than PTFE, due to its molecular structure is more compact, its crystalline structure transition temperature is higher, the temperature range is wider (0-100℃), the transition is more slow, not easy to occur fibrosis. FEP (tetrafluoroethylene-hexafluoropropylene copolymer), when the content of hexafluoropropylene is low, its condensed matter structure is the same as PTFE, with four crystal transformation zones II, IV, I, III, when the content of hexafluoropropylene is high, the crystal transformation near room temperature does not pass through the IV zone, from the II zone to the I zone, due to the intervention of $-CF_3$ in hexafluoropropylene, the crystal zone disorder increases. The crystallinity and mechanical properties of the polymer are reduced. The application of dispersed polymerized PTFE in the dry electrode mainly depends on the following characteristics: (1) the fibrotic characteristic, PTFE has 4 crystal transformation regions, the intermolecular van der Waals force is low, and the fibrosis can occur at a temperature lower than room temperature; (2) The molecular weight of dispersed polymerized PTFE is higher, generally millions or even tens of millions, which can form longer fibril; (3) PTFE material is inert and resistant to (electrolyte) corrosion; (4) High crystallinity and good mechanical properties. By comparison, PTFE is the best bonding agent for dry electrode process.

In summary, the dry electrode process for PTFE applications not only eliminates the use of NMP solvents, manufacturing more green, but also reduce manufacturing costs, achieve high energy density of the cell, help realize all-solid-state battery technology and pre-lithium technology, hereby apply for exemption from the restrictions on the application of PTFE in the dry electrode.

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