Application for Derogation from PFAS Restrictions for Specific Uses in BATTERIES

Introduction

Battery Association of Japan (BAJ) represents primary and rechargeable battery industries in Japan. It consists of 15 regular members most of which are battery manufacturers in Japan and 95 supporting members such as material suppliers, sales company of overseas battery brands, etc.

BAJ believes that the PFAS restriction proposal this time is an excessive measure, as it seeks to collectively restrict over 10,000 PFAS on the ground of persistence alone. PFAS are essential materials for batteries, and the impact of not being able to use them would be immeasurable. BAJ requests derogation for 13.5 years by the following description about the actual use of PFAS in batteries, the alternatives feasibility, and the economic and social impacts.

I. Type of PFAS and annual tonnage for the relevant use.

< Lithium-ion battery > Electrode binder, polymer electrolyte, separator

・PVDF (polyvinylidene fluoride, CAS 24937-79-9) is used in the electrodes, polymer electrolytes and separators of lithium-ion batteries. In particular, PVDF is used in almost all lithium-ion batteries for electrodes.

(1) Annual use tonnage

・As described in A. 3.13. 2 in Annex A to PFASs restriction proposal report, if the volume of lithium-ion batteries is set at 157 000 t/y based on the data of the Urban mine platform (as of 2022/12/16) and the polymer PFAS content in the batteries is set at 1%, the volume of polymer PFAS used in lithium-ion batteries is calculated to be 1600 t/y. If the energy density of a lithium-ion battery is set at 200Wh/kg, a quantity of 157 000 t/y of lithium-ion batteries is equivalent to 31.4GWh/y.

According to the description in Table A.6 in Annex A to PFASs restriction proposal report, total production of PVDF is estimated at 15 000 -20 000 t (2019) in the EEA and 80 000 t (2022) globally.

(2) Future Forecast

・According to the JRC report, global lithium-ion battery sales are projected to be 250~1 100GWh in 2030 (Europe's share of production is 5~25%) and 600~4000GWh in 2040. (See Citations [1] and [2]) In the case of 4000GWh/y, the amount of polymer PFAS used is calculated to be 200 000 t/y by the same calculation as above.

[1] "Lithium-ion batteries for mobility and stationary storage applications," JRC
https://visitors-centre.jrc.ec.europa.eu/sites/default/files/poster_flyer/jrc114616_li-ion_batteries_two-pager_final.pdf

[2] "Li-ion batteries for mobility and stationary storage applications," JRC 2018
https://publications.jrc.ec.europa.eu/repository/bitstream/JRC113360/kjna29440enn.pdf

<Lithium-ion battery> Gasket

・PFA (perfluoroalkoxyalkane, CAS 26655-00-5) is used in the gasket of lithium-ion batteries.

(See Section V Attachment 1 on the annual use tonnage)

<Lithium-ion battery> Electrolyte additive
LiTFSI (Lithium bis (trifluoromethanesulfonyl) imide, CAS 90076-65-6) and fluorobenzene（CAS 462-06-6）are used as additives in electrolytes for lithium-ion batteries.
(See Section V Attachment 1 on the annual use tonnage)

<Lithium-ion battery> Module parts
PTFE (polytetrafluoroethylene, CAS 9002-84-0) is used in module parts of lithium-ion batteries.
(See Section V Attachment 1 on the annual use tonnage)

<Nickel metal hydride battery/Nickel Cadmium battery> Positive electrode binder
PTFE (polytetrafluoroethylene) and TEE-FP copolymers (poly(propylene-co-tetrafluoroethylene), CAS 27029-05-6) are used as positive electrode binder for Nickel metal hydride battery and Nickel Cadmium battery.
(See Section V Attachment 1 on the annual use tonnage)

<Nickel metal hydride battery/Nickel Cadmium battery> Negative electrode
Powders of fluororesin such as PTFE (polytetrafluoroethylene), FEP (tetrafluoroethylene hexafluoropropylene copolymer, CAS 25067-11-2) and PFA (perfluoroalkoxyalkane) are used on the negative electrode surfaces of Nickel metal hydride battery and Nickel Cadmium battery.
(See Section V Attachment 1 on the annual use tonnage)

<Lithium primary battery> (CR type/BR type, cylindrical shape and coin shape)
PTFE (polytetrafluoroethylene), ETFE (tetrafluoroethylene-ethylene copolymer, CAS 25038-71-5), FEP (tetrafluoroethylene-hexafluoropropylene copolymer) are used as positive electrode binder for lithium primary batteries (CR/BR type, cylindrical and coin shapes).
(See Section V Attachment 1 on the annual use tonnage)

<Lithium primary battery> (Lithium thionyl chloride battery)
PTFE (polytetrafluoroethylene) is used as a positive electrode binder for lithium primary batteries (ER type).
(See Section V Attachment 1 on the annual use tonnage)

<Lithium primary battery> (CR cylindrical)

LiTFS (lithium trifluoromethanesulfonate, CAS 33454-82-9) and LiTFSI (lithium bis(trifluoromethanesulfonyl)imide) are used as electrolytes in CR cylindrical lithium primary batteries.

(See Section V Attachment 1 on the annual use tonnage)

<Alkaline button battery>

PTFE (polytetrafluoroethylene) is used in the positive electrode binder of alkaline button battery (LR and SR).

(See Section V Attachment 1 on the annual use tonnage)

<Coin-shape lithium rechargeable battery> Positive electrode binder

PTFE (polytetrafluoroethylene), ETFE (tetrafluoroethylene-ethylene copolymer), FEP (tetrafluoroethylene-hexafluoropropylene copolymer), PVDF (polyvinylidene fluoride) are used as positive electrode binders for coin-shape lithium rechargeable battery.

(See Section V Attachment 1 on the annual use tonnage)

<Coin-shape lithium rechargeable battery>

FA (perfluoroalkoxyalkane) is used in gaskets for coin-shape lithium rechargeable battery.

(See Section V Attachment 1 on the annual use tonnage)

<Coin-shape lithium rechargeable battery>

LiTFSI (lithium bis(trifluoromethanesulfonyl)imide) is used as an electrolyte for coin-shape lithium rechargeable battery.

(See Section V Attachment 1 on the annual use tonnage)

PFAS used in batteries and their relevant use are summarized in the table below.

Battery	PFAS	The relevant use
Li-ion	PVDF	Electrode binder, polymer electrolytes, separators
	PFA	Gasket
	LiTFSI, Fluorobenzene	Electrolyte additive
	PTFE	Module parts

Ni-MH, Ni-Cd	PTFE TEE-FP Copolymer	Positive electrode binder
	PTFE FEP PFA	Negative electrode
Lithium primary battery (CR/BR, cylindrical and coin shape)	PTFE, FEP, PFA	Positive electrode binder
Lithium primary battery (ER)	PTFE	Positive electrode binder
Lithium primary battery (CR cylindrical)	LiTFS, LiTFSI	Electrolyte
Alkaline button battery (SR & LR)	PTFE	Positive electrode binder
Coin-shape lithium rechargeable battery	PTFE, ETFE, FEP, PVDF	Positive electrode binder
	PFA	Gasket
	LiTFSI	Electrolyte

II. The key functionalities provided by PFAS for the relevant use.

<Lithium-ion battery> PVDF (PVDF for electrode and PVDF for polymer electrolyte)

It is used as an electrode in lithium-ion batteries, mainly for the purpose of maintaining an electrically and structurally bound electrode active material powder and current collecting metal foil (binder). Electrode binders for batteries are required to have many functions, such as mechanical strength, adhesion, chemical and electrochemical stability, solubility in organic solvents, and electrolyte swelling. In particular, the inside of the positive electrode of a lithium-ion battery is exposed to a strong oxidizing atmosphere, so extremely high oxidation resistance and electrochemical stability are required to meet the long-term durability performance requirements of over 10 years required for LIBs. No alternative to PVDF has been established as a material that provides a balanced coverage of these performances. That's why PVDF is used as a binder for lithium-ion batteries in almost all products produced around the world today.

・In addition, the polymer electrolyte LIB battery has the advantage of using PVDF as a binder for the positive and negative electrodes, so that the electrode and the electrolyte are integrated and can be rigid as a battery so that the shape can be stabilized even after charging and discharging. In addition, by ensuring ionic conductivity and retaining the electrolyte, the polymer electrolyte LIB battery has no leakage even with the laminate exterior, and is more safe than the conventional liquid electrolyte LIB, making it a necessary battery for applications requiring high safety. Therefore, it is difficult to substitute polymers other than PVDF that can achieve both safety and performance. (See references [3], [4], [5], [6] and [7)

[3] Polymer Gel Electrolyte Lithium-Ion Secondary Battery Development Technology
https://www.jstage.jst.go.jp/article/electrochemistry/76/7/76_7_493/_pdf/-char/en

[4] "Laminate-type Lithium-ion Polymer Battery," Tohoku Murata Manufacturing Co., Ltd.
https://corporate.murata.com/en-global/group/tohokumurata/quality/quality01

[5] "[Battery materials] Vol.2 Binder for lithium-ion batteries," DAIKIN
https://www.daikinchemicals.com/magazine/column-lithium-ion-battery-02.html

[6] "Applications of Polyvinylidene Fluoride (PVDF) for LIB Materials"
https://www.jstage.jst.go.jp/article/gomu/92/11/92_410/_pdf/-char/ja

[7] "PVDF Separator Coatings," Arkema Global Website
https://hpp.arkema.com/en/markets-and-applications/renewable-energy/lithium-ion-battery/separator-coatings/

<Lithium-ion battery> PVDF (PVDF for separator)

・The square can exterior and laminate exterior are mass-produced with liquid electrolytes, but the use of a separator surface with PVDF provides shape stabilization during charging and discharging. (See citation [8]) These realizations are due to the unique properties of PVDF in terms of solvent resistance, heat resistance, electrochemical stability, and adhesion, and there is no alternative.

[8] Research & Development ”Separators for Lithium-ion Batteries”, TEIJIN
https://www.teijin.com/rd/technology/separator/

<Lithium-ion battery > Gasket

PFA is used in the gasket of lithium-ion batteries. The gasket has the function of electrically insulating the positive and negative terminals and sealing them to prevent air and moisture from passing through the battery container.

The gasket is always present in a location exposed to the cell's internal and external environment.

To maintain functional airtightness, the gasket must have high chemical stability that is not altered by the electrolyte inside the battery.

There are many welding processes in the manufacturing process of lithium-ion batteries, and it is essential to have high heat resistance that maintains shape and performance even at high temperatures generated during welding near gaskets. In addition, high heat resistance is also required for heat generation due to charging and discharging during use.

As for the above basic functions, it is required to have the performance for a long period of 10 years or more from the viewpoint of suppressing the performance degradation of the product and ensuring safety. The gasket with PFA is the only material that simultaneously meets the chemical stability, high heat resistance and durability required to maintain high airtightness.

<Lithium-ion battery> Electrolyte additive

Fluorinated materials such as LiTFSI and fluorobenzene, which are used in the electrolyte of lithium-ion batteries, have excellent oxidation resistance and can suppress interfacial side reactions, so they are indispensable for further performance improvement (higher voltage and higher capacity) and safety assurance of lithium-ion batteries.

<Lithium-ion battery> Module parts

PTFE is used in module parts of lithium-ion batteries as a material that has multiple properties such as oil repellency, water resistance, air permeability, heat resistance, chemical resistance, and weather resistance.

<Nickel metal hydride battery/Nickel Cadmium battery> Positive electrode binder

In Nickel metal hydride battery, an active material particle filled on a foamed nickel substrate (non-sintered type) is widely adopted as a positive electrode, where fluororesin-based binders such as PTFE and TFE-PP copolymers are used. When alternative materials, such as hydrocarbon-based rubber (SBR, etc.) and hydrophilic polymers (polyacrylic acid, etc.), are used as positive electrode binders, the binder molecules are unable to withstand the strong oxidation potential in a strong alkaline solution during battery charging, resulting in a decomposition reaction (formation of carbonate ions in the solution). It has been confirmed that the corrosion of the negative electrode hydrogen storage alloy is accelerated by the presence of carbonate ions. In addition, the loss of the positive electrode active material from the substrate also increases, and the cycle life characteristics of the battery are greatly reduced for the above two reasons. Therefore, only fluororesin -based binders stable against oxidation potential can be used.

<Nickel metal hydride battery/Nickel Cadmium battery> Negative electrode

・Fluororesin powders such as PTFE, FEP and PFA are applied to the negative electrode surfaces of Nickel Cadmium battery and Nickel metal hydride battery to provide water repellency. As a result, when gas is generated from the positive electrode during overcharging, a three-phase boundary of gas, liquid and solid is formed on the surface of the opposing negative electrode, allowing gas absorption to proceed smoothly and suppressing the rise in the internal pressure of the battery.

<Lithium primary battery> (CR type/BR type, cylindrical shape and coin shape)

PTFE, ETFE, and FEP used in positive electrode binders have the following functions.

① Basic function as a binder that integrates the mixture (mixed particles of active material, conductive material, etc.) in the press process of positive electrode production and maintains the mechanical strength of the electrode over the long product life cycle.

② In order to fully demonstrate the performance, it is important to contain as little water as possible during battery assembly. They have enough heat resistance and oxidation resistance not to deteriorate in this process. In addition, we have research knowledge that the long-term reliability of the battery deteriorates to about 1/4 when the drying temperature is set to less than 200°C.

(See Section V Attachment 2 Document 4)

③ In the battery, a high potential (about 3 V) of the positive electrode is applied while being immersed in the organic electrolyte. They have chemical resistance and electrochemical stability that does not oxidize and decompose in such an environment.

<Lithium primary battery> (Lithium thionyl chloride battery)

PTFE used in positive electrode binder has the following functions.

① A porous electrode is important for the positive electrode of ER battery because it traps and contains thionyl chloride, a liquid active material. When the carbon of conductive material and PTFE are kneaded, the PTFE fibrillates and integrates between the carbon powders, thus functioning as a binder that forms a suitable porous electrode.

② In order to fully demonstrate the performance, it is important to make the battery as free from moisture as possible, and it is necessary to remove the moisture absorbed by the carbon at a high temperature of 200°C or higher when manufacturing the positive electrode. PTFE has heat resistance that does not degrade in this process.

③ PTFE is chemically stable against highly reactive thionyl chloride. This makes it possible to maintain the mechanical strength of the electrode over the product life cycle.

<Lithium primary battery> (CR cylindrical)

LiTFS and LiTFSI, which are used as electrolytes in CR cylindrical lithium primary batteries, have the following functions.

① They have basic function as an electrolyte that easily dissolves in the electrolytic solution and provides high ionic conductivity over wide temperature range.

② In the battery, they do not cause side reactions (oxidation, dissolution, etc.) with manganese dioxide, which is the positive electrode active material, and the SUS material of the current collector and case, ensuring long-term battery reliability.

③ Even if the battery is in an abnormal state such as over-discharge, they do not generate a large amount of heat, ensuring the safety of the battery.

<Alkaline button battery>

PTFE, which is used as a positive electrode binder for alkaline button batteries, has the functions of oxidation resistance, chemical resistance (alkaline resistance), and electrochemical stability in addition to its basic function of binding.

For example, in the case of the LR system, manganese dioxide is used as the positive electrode active material, but this manganese dioxide electrode swells when immersed in the electrolyte for a long time without PTFE, and the strength after immersion in the electrolyte decreases to 30% or less. As for the battery performance, it causes an increasing impedance and a liquid leakage phenomenon.

(See Section V Attachment 2 Document5)

<Coin-shape lithium rechargeable battery>

PTFE, ETFE, FEP, and PVDF used in positive electrode binders have the following functions.

① They have a basic function as a binding agent that integrates the positive electrode mixture (mixed particles of active material, conductive material, etc.) and maintains the mechanical strength of the electrode over the subsequent long-term product life cycle.

② In order to fully demonstrate the performance, it is important to contain as little water as possible during battery assembly. They have enough heat resistance and oxidation resistance not to deteriorate in this process.

③ In the battery, the charging voltage of the positive electrode is applied while being immersed in the organic electrolyte. They have chemical resistance and electrochemical stability that do not oxidize and decompose in such an environment.

<Coin-shape lithium rechargeable battery>

PFA used in gaskets has water repellency, chemical resistance, and oxidation resistance (durability) in addition to its basic function of sealing. A coin-shape lithium rechargeable battery with a small capacity tends to suffer from a decrease in performance when moisture enters the inside of the battery from the sealed portion (as compared to cylindrical lithium-ion battery). Therefore, PFA resin, which does not deteriorate over a long period of time and maintains high water repellency, is the most suitable gasket material.

<Coin-shape lithium rechargeable battery>

LiTFSI, which is used as an electrolyte exhibits high ionic conductivity and high safety functions derived from C-F bonds compared to general-purpose electrolytes (such as LiPF6). By using this electrolyte, it is possible to ensure the large current discharge characteristics and safety of the coin-shape lithium rechargeable battery.

III. The number of companies in the sector estimated to be affected by the restriction.

16 battery manufacturers related to this field are included in BAJ members. This number increases to 110 including peripheral companies such as material manufacturers. Many of them will be affected if batteries cannot be produced due to the PFAS restrictions.

IV.Regarding the technical feasibility of alternatives

<Lithium-ion battery> PVDF (for electrode binder)

・Although alternatives to PVDF are also being considered, fluorine-based materials are currently the only practical binders that can ensure battery characteristics in a charged state in lithium-ion batteries, especially in systems using layered oxide positive electrodes, and it is not easy to apply alternatives. At present, there is no substitute material that meets all the requirements of PVDF: solvent resistance, heat resistance and electrochemical stability, adhesion to active materials and current collectors, and paint properties required for electrode application. (See citations [9], [10], [11] and [12]) There's no hope of finding one in a few years. Acrylic and cellulosic binders are available as non-PFAS binders. They have low electrochemical stability at high noble potentials, so they can not be used for positive electrodes. The latest LIB development, on the other hand, is a dry electrode, which also uses PFAS materials, according to the cited document [13].

[9] Applications of Polyvinylidene Fluoride (PVDF) for LIB Materials

https://www.jstage.jst.go.jp/article/gomu/92/11/92_410/_pdf/-char/ja
[10] Lithium-ion Batteries , Springer (Chapter 6 P155~P161), Y, Ralph J. Brodd, Aisaku Nagai,
[11] "Solef® PVDF Improves Battery Performance," SOLVAY
https://www.solvay.com/en/brands/solef-pvdf/li-ion-batteries
[12] "PVDF Electrode Binders," Arkema Global Website
https://hpp.arkema.com/en/markets-and-applications/renewable-energy/lithium-ion-battery/electrode-binders/

[13] Brandon Ludwig, Zhangfeng Zheng, Wan Shou, Yan Wang & Heng Pan "Solvent-Free Manufacturing of Electrodes for Lithium-ion Batteries" SCIENTIFIC REPORTS
https://www.nature.com/articles/srep23150.pdf

・Research on potential alternatives to water-based binders using non-PFAS has been active, but triangular-type active materials, which are widely used for EVs in particular, are susceptible to performance by moisture, and this essential problem has not been solved. For ternary positive polar active materials, the effects of moisture are as follows: 1) Li abstraction from the active material, 2) continuous LiOHaq formation and structural breakdown of the powder surface, 3) subsequent pH increase, and 4) consequent corrosion of Al current collectors. These lead to essential performance degradation. (See references [14], [15] and [16])

・In addition, although it has been reported that the initial performance and simple cycle-life performance of LFP-based positive electrodes are comparable to those of PVDF-used products, most of the results of lab-scale experiments on the order of several grams or on thin films have not been verified for performance and manufacturability at the actual product level, which is necessary to completely determine suitability as a new binder. (See references [14], [15] and [16])

[14] Dominic Bresser, Daniel Buchholz, Arianna Moretti, Alberto Varzi and Stefano Passerini "Alternative binders for sustainable electrochemical energy storage – the transition to aqueous electrode processing and bio-derived polymers," ROYAL SOCIETY OF CHEMISTRY
https://pubs.rsc.org/en/content/articlehtml/2018/ee/c8ee00640g

[15] Yue Ma, Jun Ma, Guanglei Cui ”Small things make big deal: Powerful binders of lithium batteries and post-lithium batteries,” Energy Storage Materials Volume 20, July 2019, Pages 146-175
https://www.sciencedirect.com/science/article/pii/S2405829718307475
[16] Niranjanmurthi Lingappan, Lingxi Kong, Michael Pecht ”The significance of aqueous binders in lithium-ion batterues,” Renewable and Sustainable Energy Reviews Volume 147, September 2021, 111227
https://www.sciencedirect.com/science/article/pii/S1364032121005141

・The performance of potential non-PFAS binder substitutes is not superior in all respects to PVDF-used products (Comparison with indicators such as initial capacity, cycle life performance and discharge rate performance) and only confirms some of the verification items that should be required for approval of mass-produced products. (See references [17], [18].)

[17] Sijiang Hu, Yu Li, Jinchao Yin, Hongqiang Wang, Ximing Yuan, Qingyu Li ”Effect of different binders on electrochemical properties of LiFePO4/C cathode material in lithium ion batteries,” Chemical Engineering Journal Volume 237, February 2014, Pages 497-502
https://www.sciencedirect.com/science/article/pii/S1385894713013715
[18] Shiyan Gao, Yuefeng Su, Liying Bao, Ning Li, Lai Chen, Yu Zheng, Jun Tian, Jian Li, Shi Chen, Feng Wu ”High-performance LiFePO4/C electrode with polytetrafluoroethylene as an aqueous-based binder,” Journal of Power Sources Volume 298, December 2015, Pages 292-298
https://www.sciencedirect.com/science/article/pii/S0378775315302287?via%3Dihub

・It has been shown in the cited document [19] that the interaction with the -OH group in the exposed part of the LFP surface causes the slurry to gel, which can be a major manufacturing problem in the fabrication of aqueous LFP cathode.

[19] Shiyan Gao, Yuefeng Su, Liying Bao, Ning Li, Lai Chen, Yu Zheng, Jun Tian, Jian Li, Shi Chen, Feng Wu ”Gelation or dispersion of LiFePO4 in water-based slurry?,” Journal of Power Sources Volume 241, November 2013, Pages 400-403

https://www.sciencedirect.com/science/article/pii/S0378775313007106?via%3

Dihub

・Examples of alternative materials: (1) Acrylic binder: Since the method of binding to the active material is different from that of PVDF, it has been confirmed that deinsertion of lithium ions on the active material surface is difficult compared with that using PVDF, resulting in higher resistance of the battery. It is also a concern that the slurry will be difficult to handle in conventional processes because of its different properties. In addition, few manufacturers mass-produce acrylic binders, raising concerns about procurement and cost.

・Examples of alternative material candidates (2) Aliphatic hydrocarbon polymers (polyethylene, polypropylene, etc.): They are not substitutable because their adhesive strength is lower than that of F-containing polymers such as PVDF. In addition, these aliphatic hydrocarbon polymers are less stable at high electric potentials compared to F-containing polymers, and they decompose, degrading the performance of batteries and making them impractical. In addition, since it is a non-polar polymer, it does not solvate, resulting in a significant decrease in productivity.

・Examples of alternative material candidates (3) Hydrophilic polymers (Polyvinyl alcohol, polyacrylic acid, polymethacrylic acid, etc.): Although they can be used as pastes in solvents such as NMP due to their polarity, their adhesiveness is significantly reduced compared to F-containing polymers. In addition, the hydrophilic functional group influences the stability of the polymer at high electric potential, which is significantly lower than that of the F-containing polymer, making it impractical.

・Examples of alternative material candidates (4) Celluloses (Methyl cellulose, ethyl cellulose, carboxymethyl cellulose, etc.): At high potentials, the stability is good compared to other polymer materials (except for F-containing polymers), but the adhesiveness is significantly reduced compared to F-containing polymers, making them impractical.

・Examples of alternative material candidates (5) Common rubbers (Natural rubber, nitrile rubber, silicone rubber, urethane rubber, butyl rubber, etc.): Adhesiveness is good compared to other polymer materials (except F-containing polymers), but stability at high potential is significantly reduced compared to F-containing polymers, making them impractical.

<Lithium-ion battery> PVDF (PVDF for polymer electrolyte)

PVDF polymer electrolyte LIB(Lithium ion battery) uses PVDF as a binder for the positive and negative electrodes, so the electrode and electrolyte are integrated into a rigid battery that can be charged and discharged to stabilize the shape of the battery. In addition, by ensuring ionic conductivity and retaining the electrolyte, the polymer electrolyte LIB battery is safe compared with the current liquid electrolyte LIB because there is no leakage even in the laminate exterior, and the use of solvents with only high boiling point solvents and the suppression of lithium dendrites on the negative electrode are also possible, making it a necessary battery for applications where high safety is required as shown in the cited references [20], [21], [22], [23], [24] and [25]. Therefore, it is difficult to substitute polymer electrolytes other than PVDF, which can achieve both safety and performance.

[20] Journal of Power Sources, 174 (2007) 1036–1040
https://reader.elsevier.com/reader/sd/pii/S0378775307013067?token=E0DADEB7C1BF3E6E15481020FB8F98EE49A4E587814B93AB2635941CDC9FFBAB957E09559E6DFE36A47349D28DE705E7&originRegion=us-east-1&originCreation=20230426002227
[21] Journal of Power Sources, Volume 406, 1 December 2018, Pages 63-69
https://reader.elsevier.com/reader/sd/pii/S037877531831084X?token=14AB0272D866CFA73D257629E24803FE4F2C3C685EF52AF0A39956C01F35808C263C13E58B0690FC32C4C15145889147&originRegion=us-east-1&originCreation=20230508015554
[22]Polymer Gel Electrolyte Lithium-Ion Secondary Battery Development Technology
https://www.jstage.jst.go.jp/article/electrochemistry/76/7/76_7_493/_pdf/-char/en
[23] "Laminate-type Lithium-ion Polymer Battery," Tohoku Murata Manufacturing Co., Ltd.
https://corporate.murata.com/en-global/group/tohokumurata/quality/quality01
[24] "[Battery materials] Vol.2 Binder for lithium-ion batteries," DAIKIN
https://www.daikinchemicals.com/magazine/column-lithium-ion-battery-02.html
[25] "Applications of Polyvinylidene Fluoride (PVDF) for LIB Materials"
https://www.jstage.jst.go.jp/article/gomu/92/11/92_410/_pdf/-char/ja
<Lithium-ion battery> PVDF (PVDF for separator)

It has been mass-produced with liquid electrolytes in square can exterior and laminate exterior, but the use of PVDF on the separator surface achieves the maintenance of charge-discharge cycle characteristics and shape stabilization during charging and discharging, and is essential especially for laminated exterior with low exterior strength and high energy density batteries, as shown in the citations [26], [27], [28], [29] and [30].These realizations are due to the solvent-resistance, heat-resistance, electrochemical stability, and adhesive properties of PVDF, and there are no alternatives. On the other hand, in the case of a cylindrical battery in which the electrode and the separator are wound in a circular shape, the adhesion between the electrode and the separator is high, and the shape can be stabilized during charging and discharging, so it is possible to use a battery other than PVDF.

[26] Research & Development ”Separators for Lithium-ion Batteries”, TEIJIN https://www.teijin.com/rd/technology/separator/

[27] Polyfile2012.4_Vol49No578

[28] Functional Material 2021.10_Vol41No10

[29] ”PVDF Separator Coatings,” Arkema Global Website https://hpp.arkema.com/en/markets-and-applications/renewable-energy/lithium-ion-battery/separator-coatings/

[30] B3 report 18-19/Chapter 5, B3 report 18-19/Chapter 11

<Lithium-ion battery> Gasket

PP is a possible alternative, but because of its low heat resistance, it will have potential defects due to high temperatures during welding. It is not realistic to ensure long-term reliability in the operating condition environment with heat generation such as high rate discharge.

<Lithium-ion battery> Electrolyte additive

Although LiTFSI and fluorobenzene are used as electrolyte materials, it is known technically that the performance of peripheral derivatives can not be guaranteed, and there is currently no substitute in terms of cost.

<Lithium-ion battery> Module parts

PTFE is used in module parts of lithium-ion batteries as a material that has multiple properties such as oil repellency, water resistance, air permeability, heat resistance, chemical resistance, and weather resistance. As a material having some of the above properties, there is high-density PE, but its properties are insufficient to replace PTFE.

<Nickel metal hydride battery/Nickel cadmium battery> binder
As an alternative to PTFE and TEE-FP copolymers used in the positive electrode binders of Nickel metal hydride battery and Nickel Cadmium battery, for example, when hydrocarbon-based rubbers (SBR, etc.) or hydrophilic polymers (polyacrylic acid, etc.) are used, the binder molecules can not withstand the strong oxidation potential in a strong alkaline solution during battery charging, resulting in a decomposition reaction (formation of carbonate ions in the solution). It has been confirmed that the corrosion of the negative electrode hydrogen storage alloy is accelerated by the presence of carbonate ions. In addition, the loss of the positive electrode active material from the substrate also increases, and the cycle life characteristics of the battery are greatly reduced for the above two reasons.

(See Section V Attachment 2 Document 2)

Therefore, only fluororesin-based binders stable against oxidation potential can be used. Only sintered positive electrodes that do not use binders can be considered, but they are difficult to replace because of the large reduction in battery capacity.

<Nickel metal hydride battery/ Nickel Cadmium battery> Negative electrode
As an alternative to PTFE, FEP, PFA, etc., which are used for the negative electrode surface of Nickel metal hydride battery and Nickel Cadmium battery, other chemically stable water repellents in alkaline electrolytes may be carbon compounds such as graphite powder, but past studies have not been able to obtain sufficient internal pressure suppression effect, and it is difficult to substitute them.

(See Section V Attachment 2 Document 3)

<Lithium primary battery> (CR type/BR type, cylindrical shape and coin shape)

As a substitute for PTFE, ETFE, and FEP used in positive electrode binders, if we focus only on the basic function of binding, there are rubbers (styrene-butadiene rubber, etc.), celluloses (carboxymethyl cellulose, etc.), and hydrophilic polymers (polyacrylic acid, etc.).

However, none of these have the functions described below, and the long-term reliability that is a feature of lithium primary batteries is lost, so replacement is difficult.

・Heat resistance and oxidation resistance that do not deteriorate when dried (baked) at 200°C or higher.
・Electrochemical stability that do not oxidize and decompose to high positive electrode potential in the battery.

<Lithium primary battery> (Lithium thionyl chloride battery)

Rubbers (styrene-butadiene rubber, etc.), celluloses (carboxymethylcellulose, etc.), and polyolefins (polyethylene, etc.) can be considered as substitutes for PTFE used in the positive electrode binder. However, none of these have the functions described below, making it difficult to create an ER battery, making it difficult to replace them.

・Heat resistance and oxidation resistance that do not deteriorate when dried (baked) at 200°C or higher
・Chemical stability to thionyl chloride

<Lithium primary battery> (CR cylindrical)

Well-known electrolytes LiPF6, LiBF4, and LiClO4 can be considered as substitutes for LiTFS and LiTFSI in cylindrical CR batteries. However, the following findings have already been clarified, and replacement is difficult.

(See Section V Attachment 2 Document 6)

・LiPF6：A side reaction occurs with positive electrode MnO2 and current collector SUS material in the battery, and the long-term storage characteristics of the battery deteriorate by 70% or more. Types using SUS cases are prone to case corrosion.
・LiBF4：A side reaction occurs with positive electrode MnO2 and current collector SUS material in the battery, and the long-term storage characteristics of the battery deteriorate by 80% or more.
・LiClO4：When the battery is in an abnormal state such as overdischarge, the amount of heat generated is very large, and the safety of the battery is lowered. (The probability of ignition or spark during overdischarge increases.)

In addition, as objective evidence for this case, references [31] and [32] show that DSC (Differential scanning calorimetry) of electrolytes shows a large difference in exothermic behavior.

・LiClO4 (solvent PC, concentration 1.0 mol) has an exothermic start temperature of 290°C and a calorific value of 780 J/g.
・LiTFS (solvent PC, concentration 1.0 mol) has an exothermic start

temperature of 330°C and a calorific value of 100 J/g.

・LiTFSI (solvent PC, concentration 1.0 mol) has an exothermic onset temperature of 322°C and a calorific value of 270 J/g.

[31] Electrochemical Society of Japan, Battery Technology Committee, Ed.: Battery Handbook P.589-590 (2010).

[32] N.Katayama, T.Kawamura, Y.Baba and J.Yamaki: Thermal stability of propylene carbonate and ethylene carbonate-propylene carbonate-based electrolytes for use inLi cells, J.Power sources, 109, P.321-326 (2002).

<Alkaline button battery>

As an alternative to PTFE used in positive electrode binders, focusing on its basic function of binding, rubbers (styrene-butadiene rubber, etc.), celluloses (carboxymethyl cellulose, etc.), hydrophilic polymers (polyacrylic acid, etc.) is considered.

However, cellulose and hydrophilic polymers swell with water due to their hydrophilic properties, and although they are expected to function to adhere to the active material, the electrode itself swells when the battery is stored for a long time due to swelling, causing impedance increase and leakage phenomenon as battery performance. In terms of electrochemical stability, rubbers, cellulose, and hydrophilic polymers are significantly inferior to PTFE, especially on the oxidation side, as suggested by the calculation results on the HOMO-LUMO energy difference in the cited reference [33].

PTFE does not swell with water but has the characteristic of fibrillating with stress. PTFE fibers, active materials, and conductive materials are entangled and bound together to prevent impedance rise and liquid leakage. In addition, since the strength of the positive electrode can be obtained due to the fibril function, the resistance to dropping and the like is high.

The positive electrode is made by compressing the mixture particles into pellets in a mold, and the lubricity of the binder is essential to release the pellets smoothly from the mold while maintaining the cohesiveness between the particles. PTFE has the lowest coefficient of static friction of 0.04 among solids, so it is suitable for this kind of lubricity. Rubbers, celluloses, and hydrophilic polymers do not have such lubricity, and problems arise in manufacturing.

For the above reasons, it is difficult to substitute PTFE for the positive electrode binder.

[33] Lithium-ion Batteries , Springer (Chapter 6, P155～P161) Y, Ralph J. Brodd,

Aisaku Nagai.

<Coin-shape lithium rechargeable battery>

As a substitute for PTFE, ETFE, FEP, and PVDF used in positive electrode binders, if we focus only on the basic function of binding, there are rubbers (styrene-butadiene rubber, etc.), celluloses (carboxymethyl cellulose, etc.), and hydrophilic Polymers (such as polyacrylic acid) are contemplated. However, none of these have the functions described below, and the performance and reliability of the coin-shape lithium rechargeable battery are impaired, making replacement difficult.

- Heat resistance and oxidation resistance that do not deteriorate when dried (baked) at 200°C or higher
- Electrochemical stability without oxidative decomposition due to battery charging

<Coin-shape lithium rechargeable battery>

As a substitute for PFA used in gaskets, PP, which is widely used in cylindrical form, was examined. As a result, it was confirmed that the moisture permeability of the gasket resin membrane is approximately four times higher. In the high temperature and high humidity storage test, the battery using PP gasket showed an early drop in the open circuit voltage (OCV) and an early rise in the internal resistance (IR), resulting in about half of the battery capacity retention. In coin-shape lithium rechargeable battery, where the ratio of the area of the crimp portion, which is the path for water infiltration, is large relative to the amount of material in the battery, it is important to make the gasket water-repellent to prevent water infiltration. Therefore, it is difficult to replace PFA.

(See Section V Attachment 2 Document 7)

<Coin-shape lithium rechargeable battery>

LiPF6, LiBF4, and LiFSI can be cited as substitutes for LiTFSI used in electrolytes, and as a result of examining these, the duration of high-current discharge was reduced by 20% or more. Since the anion radius of LiTFSI is the largest as shown below, it is considered that the dissociation degree of Li ions is high and the ionic conductivity is high.

- LiTFSI：0.328nm

・LiPF6：0.255nm
・LiBF4：0.227nm
・LiFSI：0.283nm

Therefore, it is difficult to replace LiTFSI.

(See Section V Attachment 2 Document 8)

V. Availability of substitute products

<Lithium-ion battery>
It is difficult to replace all lithium-ion batteries with other batteries. Because the battery voltage differs greatly from that of primary batteries, simple replacement is not possible, and there is a problem of increasing waste. Nickel metal hydride battery/ Nickel Cadmium battery (nominally 1.2 volts) have very different battery voltages than lithium-ion batteries (nominally 3.6-3.7 volts), and these batteries are not replaceable because they also use PFAS. Lead-acid batteries have low energy density and are difficult to replace with lithium-ion batteries.

<Nickel metal hydride battery/Nickel Cadmium battery>
It is difficult to replace all Nickel metal hydride batteries and Nickel Cadmium batteries with other batteries. The active replacement of these batteries with alkaline batteries or carbon-zinc batteries poses the challenge of increasing waste. There are compatible lithium-ion batteries (3.6-3.7 volts) with a step-down circuit to make them 1.5 volts, but there are major problems in ensuring safety when users misuse them (reverse loading, mischarging, short-circuiting, etc.), and they are not sufficient replacements. In the first place, lithium-ion batteries themselves use PFAS, so they're no substitute. Nickel Cadmium battery and Nickel metal hydride battery do not use organic electrolytes, and because concentrated alkaline electrolytes maintain high ionic conductivity over a wide temperature range, they are widely used in industrial applications where higher safety and operation over a wide temperature range are required. Replacing the power supply for these applications with lithium-ion batteries is difficult because they do not have the above features. Lead batteries also exist as batteries using aqueous electrolyte solutions, but they are difficult to replace due to their low energy density and limited weight and footprint.

<Lithium primary battery>

When considering alkaline batteries or carbon-zinc batteries as a replacement for cylindrical lithium batteries, in addition to differences in battery voltage itself, there are significant differences in dischargeable temperature range, stability of discharge characteristics during long-term use, volume energy density (Wh/L), and weight energy density (Wh/kg), making it difficult to replace the applications for which primary lithium batteries are used. It is also difficult to replace coin lithium batteries with alkaline button batteries for the same reason as above.

<Alkaline button battery>

LR series is a general-purpose primary battery used in small, space-saving devices that cannot use normal size alkaline batteries or carbon-zinc batteries, and there is no alternative battery, including the fact that it is cheap.

SR series is characterized by flat discharge voltage and excellent load characteristics and has long been used as the optimal power supply for analog quartz watches. In recent years, some of them have been replaced by systems that combine solar cells and coin-shape lithium rechargeable batteries, but this replacement is limited due to the problem of high prices. (In addition, coin-shape lithium rechargeable batteries also contain PFAS, so the situation remains the same.) There are no alternative SR batteries other than the above.

<Coin-shape lithium rechargeable battery>

Small all-solid-state batteries (capacity of several tens of mAh or less) are being considered as an alternative candidate for some applications. These are classified into two types, oxide type and sulfide type, according to the type of solid electrolyte. Since oxide-based electrolytes have lower ionic conductivity than the liquid electrolytes in coin-shape lithium rechargeable battery, it is difficult to replace them in applications where high-rate and low-temperature discharge characteristics are important. In addition, sulfide-based materials have sufficient ionic conductivity, but PFAS such as PVDF are generally used for electrode fabrication, and the situation remains unchanged. Both all-solid-state batteries are still in the process of technological development and require new equipment and new construction methods, which poses significant cost issues and makes replacement difficult.

VI. Economic and social impacts caused by PFAS restrictions.

PFAS is used as an integral material in various batteries as shown in the table below. It is very difficult to develop alternatives, and if the use of all PFAS containing fluoropolymers is banned, it will be virtually impossible to supply these batteries to the market. The numbers are for the global market, but battery-related companies will be at risk of losing at least the European market's worth of the 80 trillion yen when the PFAS restrictions take effect. Moreover, this loss is only for the battery manufacturer, and the loss is further expanded with that of material manufacturers added.

Battery Type	WW Demand (100M JPY)		Major Application
	2020	2025	
Li-ion	194,000	689,700	Electric Vehicle, Energy Storage System
	88,200	93,700	Smartphone, PC, Power Tool
Ni-MH	1,643	2,630	Electric Vehicle, Energy Storage System
	790	682	Consumer Use
Coin Li Rechargeable	638	1,696	Earphone, Watch, Hearing Aid, IoT
Cylindrical Li Primary	536	727	Smoke Alarm for Homes, Vehicle Emergency Call, AED
Coin Li Primary	600	610	Tire Pressure Monitoring, Smart Key, Blood Glucose Meter
Li Thionyl Chloride (ER)	725	865	Smart Meter, Military Use
Alkaline Button	73	68	Toy, Thermometer, Game
Zinc Air	288	190	Hearing Aid
Total	287,493	790,868	

Source: Fuji Keizai '2022 Battery-related Market Report' (in Japanese)

In addition to corporate losses, the impact on consumers and society is enormous. Primary batteries are widely embedded in social infrastructure, such as applications in the field of daily life, vehicles, security, medical, and ICT. If these primary batteries cannot be supplied due to the PFAS restrictions, there is a risk of causing social confusion.

Lithium-ion batteries are not only the main power source for portable devices such as smartphones and PCs that are indispensable in modern life, but also a key technology essential for EVs and energy storage systems. If lithium-ion batteries become unusable due to the PFAS restrictions, the electrification of vehicles and the expansion of renewable energy, which are the pillars of the European Green Deal policy, will be significantly delayed, leading to increasing the amount of carbon dioxide and making far away the carbon-neutral goals.

That runs counter to global environmental policies that many countries have in common.

Based on the above, we request a 13.5-year derogation, as it will take at least 10 years to search for and commercialize alternatives to PFAS for batteries. In addition, since there is a possibility that a substitute product may not be found as a result of the search, it is requested that a provision for reviewing the derogation be included in the restrictions.