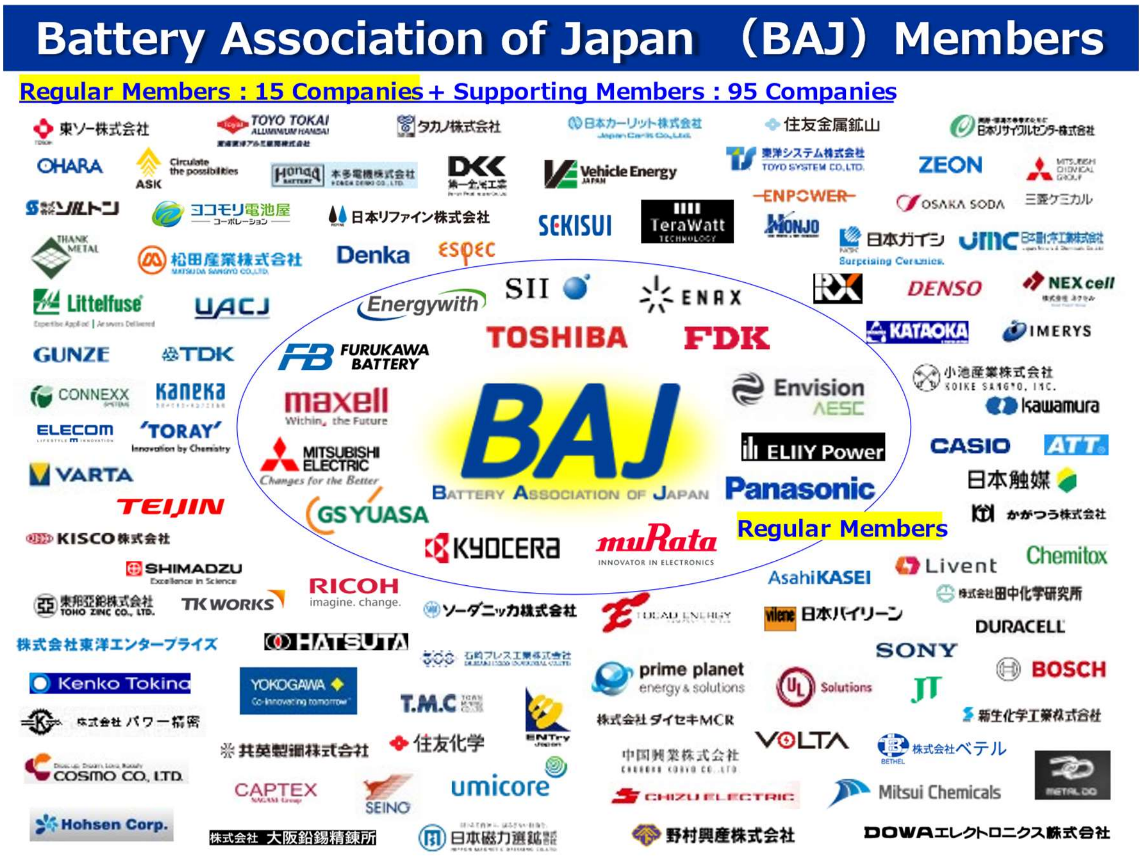
Additional Comments
from Battery Association of Japan

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 posted the first comments (ref. No.4331 dated May 30.) on info request 8, in which we presented information such as PFAS usage and key functionalities in batteries, alternatives feasibility, and economic, social impacts.

This time we aim to reinforce them by answering info request 2 (emission), 3 (incineration), and 4 (impacts on the recycling industry).

a. PFAS emissions from batteries by lifecycle

At the battery manufacturing, PFAS is contained in pieces of positive electrode processing, surplus positive electrode mixture and electrolyte, defective batteries generated in the assembly line, etc., and is collected by recyclers. At the battery using, PFAS is sealed within the battery container and no outflow occur. At the disposing, PFAS is contained in waste batteries and goes to recyclers for resource recovery.
When applying the above to figures of BAJ members' global production, the amount of PFAS contained in defective batteries, etc. at the manufacturing stage is approximately 170 tons (10%), and the amount of PFAS contained in waste batteries at the disposal stage is approximately 1,570 tons (90%).
However, PFAS emissions to the environment are considerably restrained by the current processes of battery recyclers, which we explain about in the following part of our comments.

b. Effectiveness of incineration in the waste management of PFAS

1) Disposal processes of batteries in Europe

In the past, the EU Battery Directive set targets for the collection rate of used batteries, and since they have been raised in stages, recycling of batteries has become widespread in society. There are many recyclers that specialize in batteries, and an overview of the recycling process for lithium-ion batteries (LIB) can be found in the following references.

<Ref.1> R.Sojka, Q.Pan, L.Billmann, "Comparative study of Li-ion battery recycling processes" ACCUREC Recycling GmbH, Sep. (2020).
https://accurec.de/wp-content/uploads/2021/04/Accurec-Comparative-study.pdf

<Ref.2> A.Rensmo, E.K.Savvidou, I.T.Cousins, X.Hu, S.Schellenberger, J.P.Benskin, Environmental Science: Processes & Impacts 25 (2023) 1015-1030.
https://pubs.rsc.org/en/content/articlehtml/2023/em/d2em00511e#cit54

According to these, the recycler process converts the battery into black mass (active mass: solid residue) and gas (decomposition product) by heat treatment at about 600°C, and then melts the black mass at 1000°C or higher (pyrometallurgy) or dissolves the black mass with acid (hydrometallurgy). In some cases, heat treatment and pyrometallurgy are performed continuously.

2) Effectiveness of incineration on PVDF

In Ref.2, the chemical reaction of PVDF (PFAS used as a binder for positive electrode) in the LIB recycling process is shown as follows. PVDF is decomposed at 400-600°C during heat treatment, and the dehydrogenation reaction during decomposition is accelerated by the presence of lithium. As summarized in Fig. 4, PVDF is decomposed to inorganic substances such as HF and LiF, and organic substances such as CF_4 (minimum PFAS), CH_3F, CH_2CF_2, CH_3CH_2F (short-chain compounds: non-PFAS), $C_6H_4F_2$ and $C_6H_3F_3$ (aromatic compounds: non-PFAS). As shown on pages 21-22 of Ref.1, these decomposed products are captured by gas cleaning system in recycling plants and landfilled.

There is no occurrence of highly harmful PFAS, such as those adopted or evaluated by Stockholm (POPs) Convention, in the decomposition products of heat treatment, and the outflow of fluorine components in final landfill disposal is managed according to appropriate standards. Therefore, PFAS emissions to the environment in the LIB recycling process are currently controlled at a fairly high level.

3) Battery systems other than LIB

The above Ref.1 and Ref.2 focus on the recycling of LIB, which are produced in large quantities. Other battery systems (nickel metal-hydride batteries and various types of primary batteries) as well as the waste and defective batteries generated during the manufacturing of these systems are treated with almost the same recycling flow. Therefore, it can be inferred that PFAS emissions due to recycling of other battery systems is also sufficiently suppressed.

4) Complete mineralization by incineration of fluoropolymers

In addition to PVDF, most of the PFAS used in batteries are fluoropolymers such as PTFE, ETFE, FEP, and PFA. The behavior and emissions during thermal decomposition of fluoropolymers have been investigated and reported in detail in the following references.

<Ref.3> J.Bakker, B.Bokkers, M.Broekman, “Per- and polyfluorinated substances in waste incinerator flue gases” RIVM report (2021) 0143.
https://www.rivm.nl/bibliotheek/rapporten/2021-0143.pdf

<Ref.4> K.Aleksandrov, H.J.Gehrmann, M.Hauser, H.Matzing, D.Pigeon, D.Stapf, M.Wexler, Chemosphere 226 (2019) 898-906.
https://www.sciencedirect.com/science/article/pii/S0045653519306435

<Ref.5> G.H.Joachim, B.Andrei, A.Krasimir, B.Philipp, T.Philip, S.Michael, A.Bruno, G.Priyanga, K.Deepak, ”Pilot-Scale Fluoropolymer Incineration Study: Thermal Treatment of a Mixture of Fluoropolymers under Representative European Municipal Waste Combustor Conditions” : Document attached to comment from Gujarat Fluorochemicals GmbH to ECHA (ref. No.4587 dated June 16.)
https://echa.europa.eu/documents/10162/0d854086-fbba-12ea-094f-176dbd7a4dc5

In Ref.3, the order of thermal stability of fluoropolymers is as follows:
PTFE > PFA > FEP > ETFE > PVDF
In Ref.4, the following is shown for the thermal decomposition of PTFE.
- Decomposition of PTFE progresses at 500-650°C
- The estimated half-life of PTFE at 800°C in nitrogen and oxygen atmosphere is well below 0.1 s, and it completely decomposes within 1 s.
- High-precision analysis of 31 types of PFAS was performed on the gas generated by incineration at 870°C for 4.0 s or 1020°C for 2.7 s, simulating the incineration of PTFE in municipal waste, and no generation was observed (that is, complete mineralization progressed.)

In Ref.5, a mixture of PTFE, PVDF, and PFA is incinerated at 860°C for 2.0 s or 1100°C for 2.0 s, and analysis has confirmed that the decomposition product does not contain any volatile (1-4 carbon atoms) short-chain PFAS and 51 types of long-chain PFAS.

Based on above information, it is desirable to increase the temperature during heat treatment to about 800 to 1100°C for the battery recycling process mentioned above. As a result, complete mineralization is achieved during decomposition of the fluoropolymer, which is presumed to be a safer direction.

The analysis results of heat treatment at 800°C at a recycler in Japan are attached in Section V. The amount of harmful PFAS produced is sufficiently suppressed to less than 25 ppb, which is the proposed restriction in EU. The ideal process would be complete mineralization (decomposition to CO_2 and HF) and the resulting HF to be petrified as CaF_2 for recycling.

5) Low-molecular-weight PFAS

In addition to fluoropolymers, low-molecular-weight electrolytes with 1-2 carbon atoms (both of which contain a CF_3-SO_2 structure) also exist as PFAS used in batteries. Although there is no research data for these thermal decompositions, from the binding energy values between CF_3-SO_2 shown in Table 5 of Ref.3, these can be decomposed by heat treatment at about 600°C (or higher) in the recycling process.

c. Impacts on the recycling industry

As far as we know, with several exceptions of pyrometallurgy, European battery recyclers are mainly doing heat treatment with temperature of around 600°C.
If they need to raise this temperature to 800-1100°C, they will likely be faced with issues like furnace durability, conditional optimization, equipment investment, carbon footprint, and so on.