Advanced Materials for PFAS-Free Applications

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innovation for life

Semiconductor Sustainability

Many Opportunities to Improve Sustainability through Innovation

Topics	Challenges
Water consumption & ultra-pure water use	• High use rate • Difficult to recycle UPW waste
Process chemicals	• Chemicals are incinerated after use • Toxic & difficult to recover
Fabrication techniques	• Fundamental processes are unchanged for decades • Non-destructive processes not implemented
Carbon neutrality	• Decrease total energy consumption & GHGs • Increase percent of renewable electricity
Emissions abatement	• New equipment needed to limit emissions & HTFs • Valuable chemicals should be recycled
Processing e-waste	• Develop processing chemistries that are simple & safe • Improve recovery yields
Natural & transient electronics	• New synthesis methods with simple, green-chemistries • Enhance performance
PFAS replacement	• Identify or design non-toxic alternatives • Maintain performance relative to existing products

Landscape Assessment

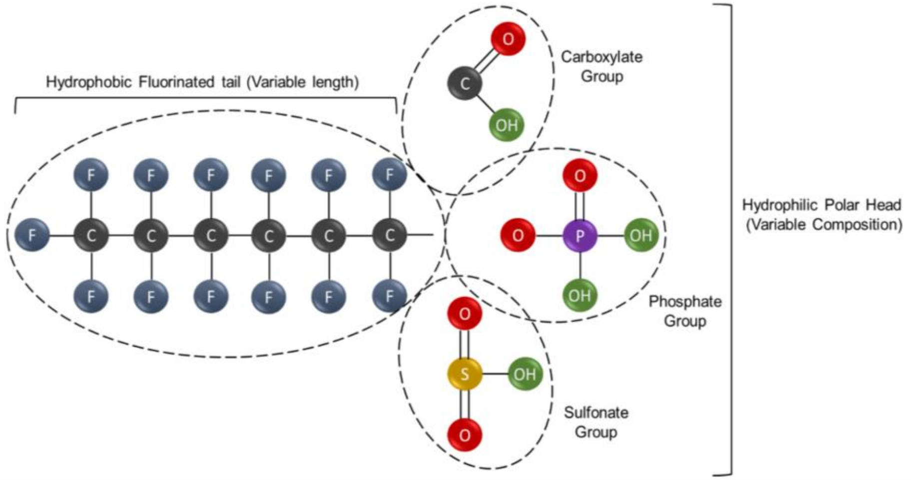
Selection based on ideal criteria for research topics

- **High urgency –** significant social & economic challenge
- **Multidisciplinary –** enables knowledge building across different disciplines
- **Diverse stakeholders –** interest from academia, industry, research institutes, and government
- **Knowledge building –** R&D can serve as foundation for policy, scientific publications, and strategic decisions
- **Tangible impact –** products & services arising from R&D are suitable for the market
- **Aligns with TNO mission -** create impactful innovations for the sustainable wellbeing and prosperity of society

Per- and polyfluoroalkyl substances (PFAS)

A constantly evolving situation

- PFAS are any substance that contains at least one fully fluorinated methyl (CF_3-) or methylene (-CF_2-) carbon atom (without any H/Cl/Br/I attached to it).[1]
    - Exact definition still under discussion
    - Generally includes hundreds to tens of thousands of chemicals[2]
    - Produced and used since the 1930s



General structure for non-polymeric perfluorinated PFAS [3]

- C–F bonds in PFAS lead to very stable substances
    - Environmentally persistent and resistant to complete degradation
    - Found in the blood of people and animals throughout the world
    - Relevant concentrations in the air, water and soil[3]

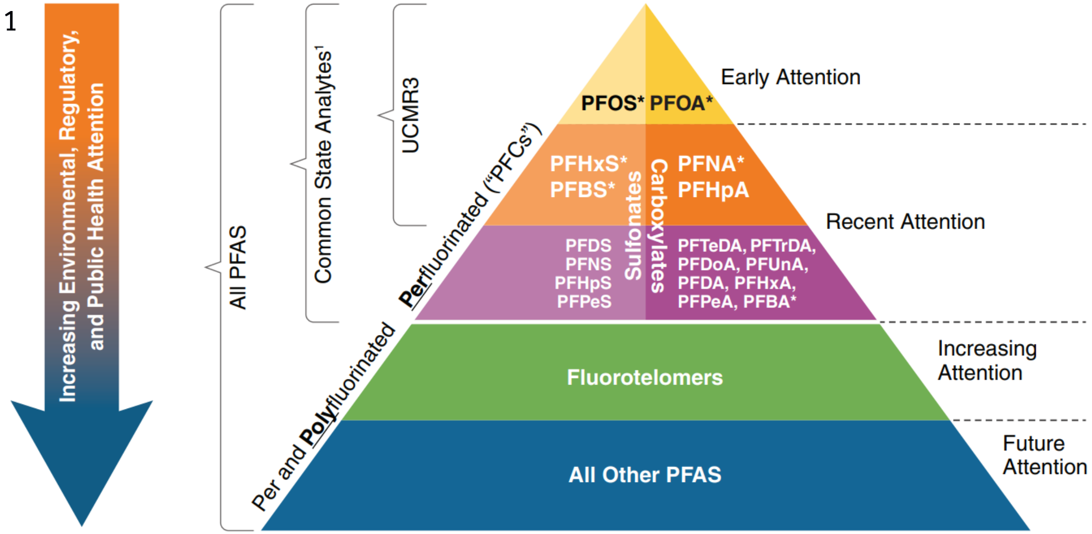
- There is no comprehensive source of information on the many individual substances[4]
    - Few (dozens) PFAS are included in environmental and biological monitoring and toxicological studies to date[2]

1. ECHA Registry of restriction intentions until outcome: https://echa.europa.eu/registry-of-restriction-intentions/-/dislist/details/0b0236e18663449b
2. Characterizing PFAS Chemistries, Sources, Uses, and Regulatory Trends in U.S. and International Markets, RTI International, 20 June 2023
3. E. Panieri, *Toxics*, 2022, 10, 44. https://doi.org/10.3390/toxics10020044
4. J. Gluge, *Environ. Sci.: Processes Impacts*, 2020, 22, 2345-2373

PFAS Regulations

Legislation naturally follows increasing public attention

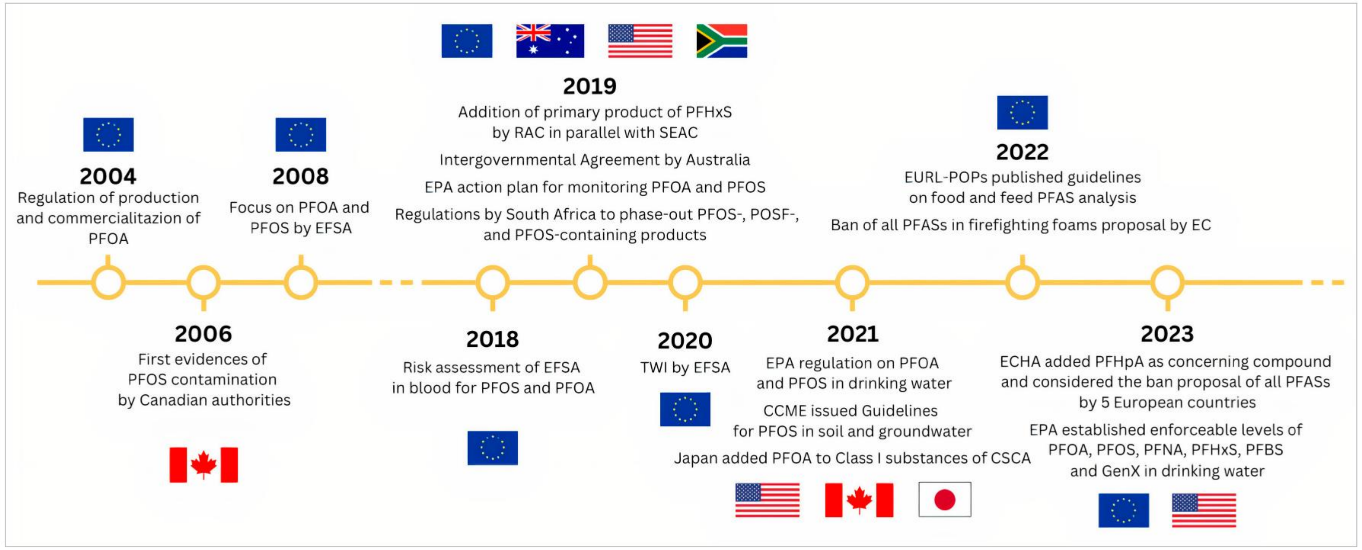
1



*Common regulatory criteria or health advisories
[1]Sum of informal poll (NJ, NH, MN)

Thematic and not proportional.
Bottom of triangle indicates additional number of compounds; not a greater quantity by mass, concentration, or frequency of detection.

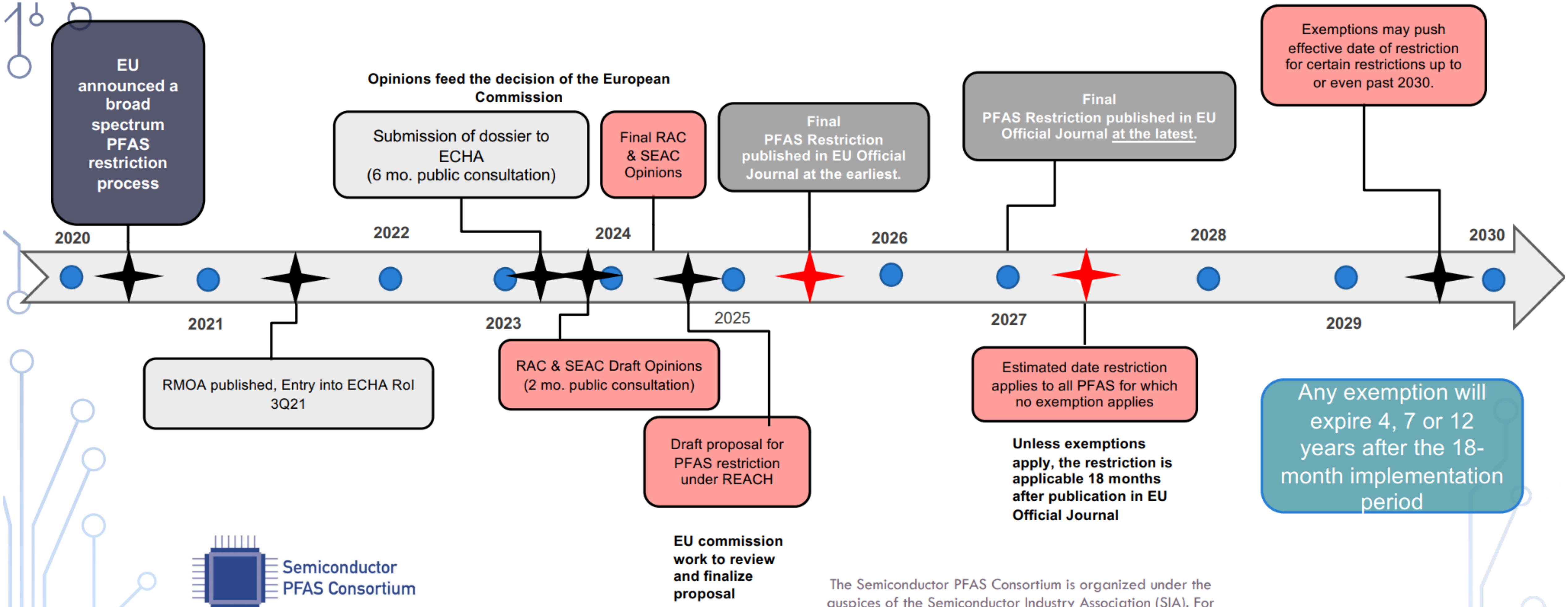
2



1. ITRC - History and Use of Per- and Polyfluoroalkyl Substances (PFAS)
2. Appl. Sci. 2023, 13, 6696. https://doi.org/10.3390/app13116696

PFAS Regulations

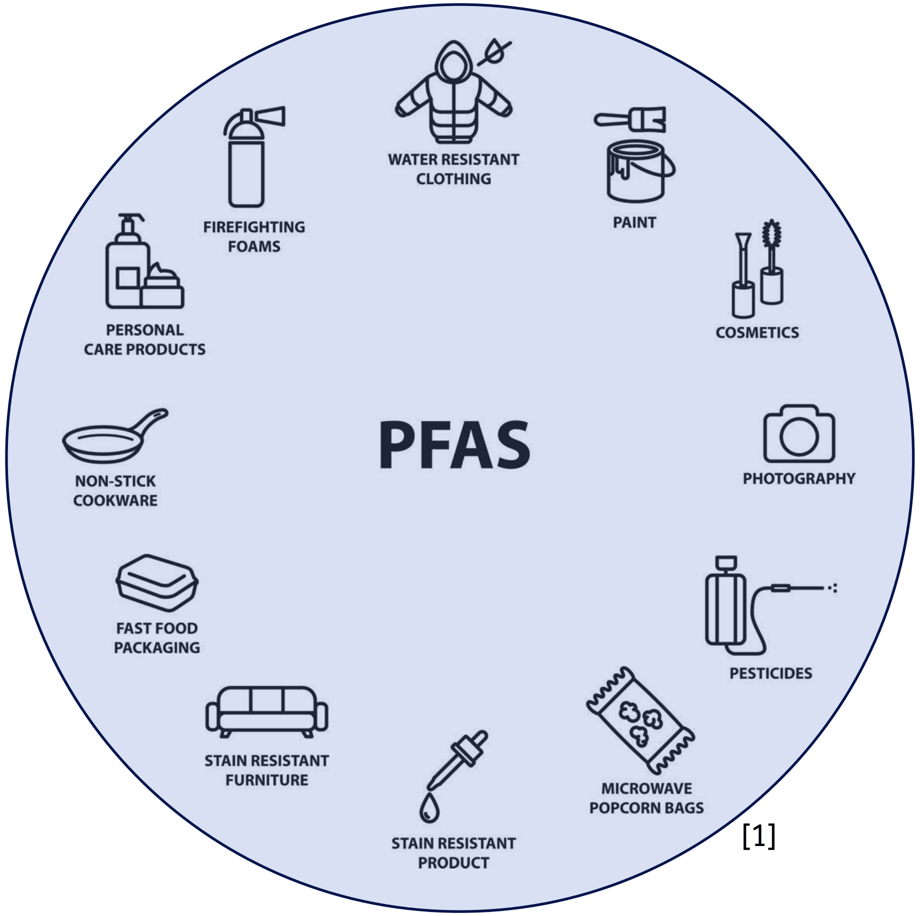
Europe REACH



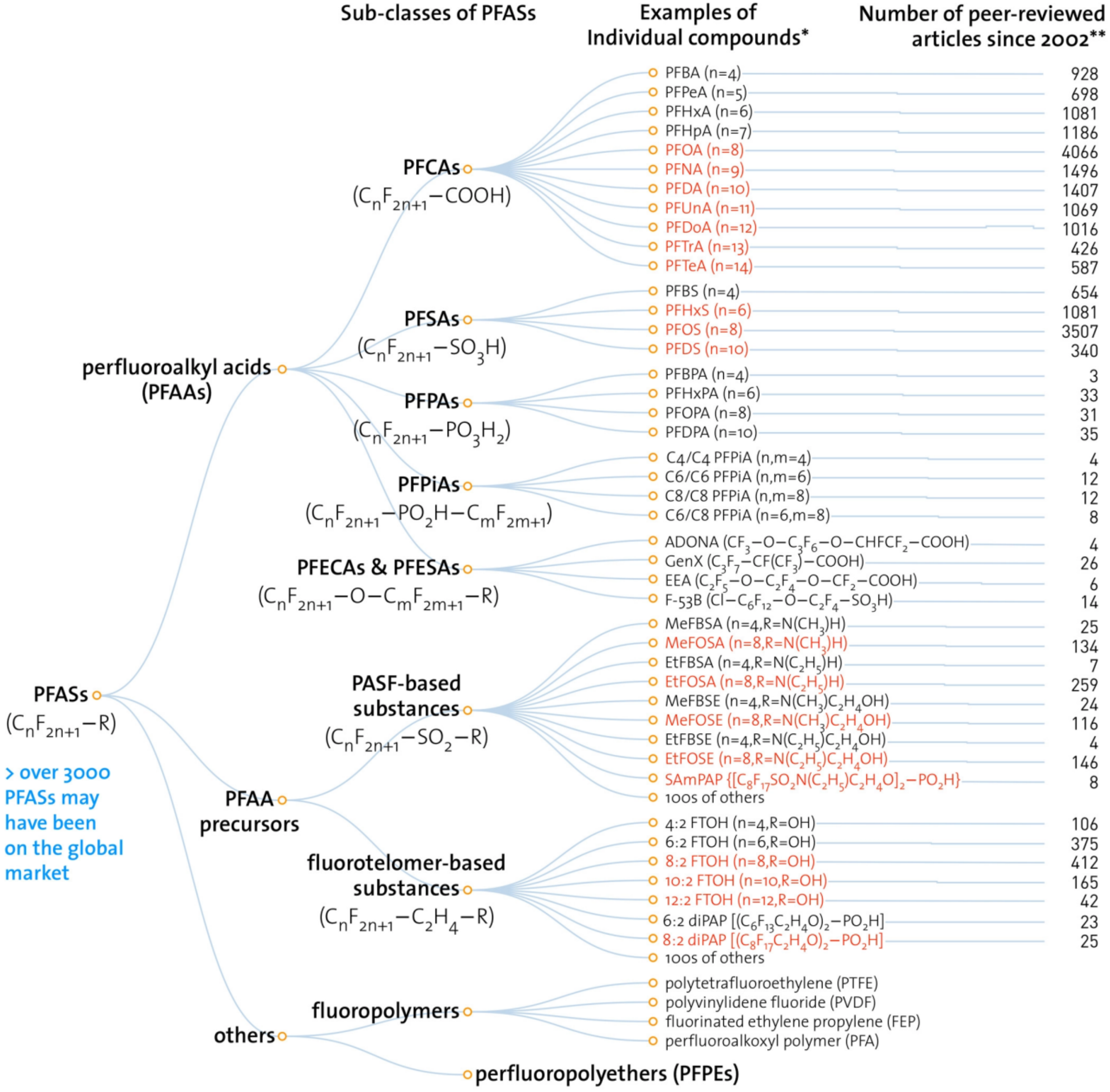
Semiconductor PFAS Consortium

The Semiconductor PFAS Consortium is organized under the auspices of the Semiconductor Industry Association (SIA). For more information, see www.semiconductors.org.

An Immense Challenge



[1]



[2]

* PFASs in **RED** are those that have been restricted under national/regional/global regulatory or voluntary frameworks, with or without specific exemptions (for details, see OECD (2015), Risk reduction approaches for PFASs. http://oe.cd/1AN).
** The numbers of articles (related to all aspects of research) were retrieved from SciFinder® on Nov. 1, 2016.

1. City of Columbus – Water protection
2. Z. Wang, Environ. Sci. Technol. 2017, 51, 2508–2518.

PFAS in Semiconductors and Electronics

Essential for a vast array of products[1,2]

- Hydrophobic coating on printed circuit boards (PCBs)
- Barrier properties and low surface energy to photoresists
- Thermal stability
- Excellent release properties
- Air is easily dissolved (eliminates trapped bubbles)
- Gaskets and seals (elastomers)
- Surfactants
  - Improve photoresist deposition/eliminate defects
  - Low refractive index and thermal/mechanical stability
- Photoacid generators (i.e. super acids) typically ≤ C4
  - No alternatives from 248 nm to EUV

2

Product	PFAS use in electronic components and manufacturing processes
Mobile devices	• Anti-smudge on touch panel • Smoothness
Printed circuit boards	• Dielectric properties • Heat resistance • Solder resistance • Low water absorption
Electric wire and cables	• Electric insulation • Dielectric properties • Molding and processing
Foldable smartphones	• Transparency • Low dielectric constant • Flexibility • Improve folding function
Electronic industry	• Testing electronic devices and equipment • Heat transfer fluids • Solvent systems and cleaning • Carrier fluid/lubricant deposition • Etching piezoelectric ceramic filters
Semiconductor industry	• Photoresistance • Photosensitivity • Increasing photosensitivity of photoresist • Generating strong acids by light irradiation • Control diffusion of acid to unexposed regions • Reducing reflection on surface • Wetting agent • Removing cured epoxy resins • Non-stick coating on carrier wafer • Bonding agent • Increase stress tolerance (fiber-reinforced fluoropolymer layer) • Separation of high voltage components (dielectric fluid) • Providing electrical signal for mechanical and thermal signals • Providing liquid crystal with dipole moment • Reducing static electricity build-up and dust attraction • Light management films in flat panel display • Cleaning integrated circuit modules • Antireflective coating

1. C. Ober, *J. Micro/Nanopattern. Mater. Metrol.*, Vol. 21(1), 2022.
2. B. Tansel, *Journal of Environmental Management* 316 (2022) 115291.

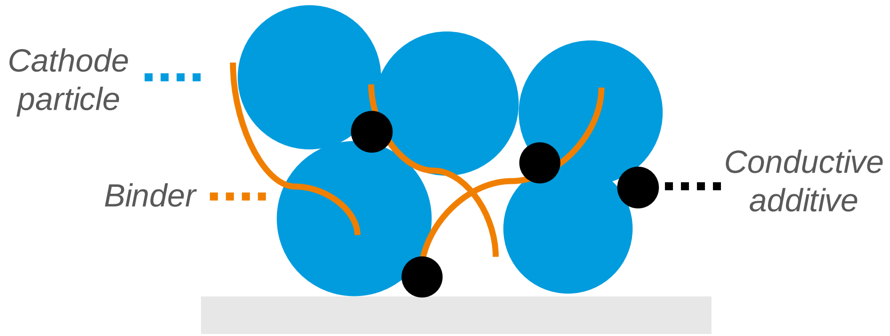
PFAS Replacement Strategy

- Take inventory of critical tools, equipment, raw chemicals, and infrastructure utilizing PFAS compounds
  - In some cases, critical items may use PFAS in their production
- Requirements must be carefully defined
  - In some cases the technical function provided by PFAS is not necessary[1]
    - Examples of sustainable material substitutions found in the cosmetics and clothing industry
  - The requirements for PFAS-based products in the semiconductor industry span a range of complexities
    - This impacts the maturity of PFAS-free alternatives as seen in photolithography
      - Surfactants & rinses, photoacid generators, photoresist polymers, reflective coatings, immersion topcoats
- Conduct a product survey using patent, scholarly, and trade literature
  - Goal is to reduce R&D time and risk
    - Identify commercial, near-commercial, or products that can be modified
- As needed, develop novel materials, chemistries, or treatments to meet unique requirements
- Establish and execute test procedure (e.g. mechanical testing, chemical analysis, off-gassing, UV resistance)

1. I. Cousins, *Environ. Sci.: Processes Impacts*, 2019, 21, 1803

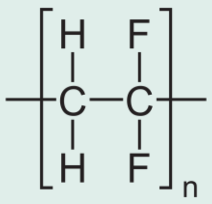
Case Study # 1

PVDF Replacement in Cathodes



Cathode composition

- Transition metal oxide particles (active material) ~90%
- Binder ~5%
- Conductive additive ~5%



PVDF – polyvinylidene fluoride

- Chemical resistivity in harsh battery environment
- Mechanical stability
- Moderate thermal stability (melting ~170-180 C)
- Questionable stability with next-gen materials
- Impossible to recycle (burning F-containing material)
- Produced from PFAS monomers

Properties of a binder:

- **Mechanical properties**
  - Binds to particles, but not too strongly
  - Flexible
  - Tensile strength, adhesion strength
- **Thermal stability**
  - Tg and melting temps
  - Battery operation temp important & processing temp
- **(Electro)chemical stability**
  - Towards oxidation, cathode active material, conductive additives
  - Not soluble in organic electrolyte
  - Soluble in slurry solvent
- **Conductivity**
  - Ionic & electronic
- **Ideal binder = flexible, suitable adhesion, good conductivity (Li, e), compatible with electrolyte, environmentally friendly.**

ENABLE Powering the Green EU Mobility

Noord Brabant Baden-Württemberg

Toward Greener and Sustainable Li-Ion Cells: An Overview of Aqueous-Based Binder Systems | ACS Sustainable Chemistry & Engineering

Alternative binders for sustainable electrochemical energy storage – the transition to aqueous electrode processing and bio-derived polymers - Energy & Environmental Science (RSC Publishing) DOI:10.1039/C8EE00640G

PVDF Replacement Strategy

Input requirements for binder candidate selection

Input for electrode fabrication

<u>**Criteria/requirements: Binder material:**</u>

- ***Max temperature of material:*** 70°C during operation, 100 – 150°C during calendaring
- ***Potential range:*** 4.9 V
- ***Physical characteristics:*** stiff below 70°C and flowable above 150°C
- ***Expansion under operation:*** 5-10% (LNMO example)
- ***Content of binder:*** 0 – 5 wt%
- ***Conductivity of binder:*** Less important (in theory better than 10^{-3} S/m²)
- Suitable for blade casting in liquid systems/wet-route (near-term approach)
- Suitable for dry-route process (longer-term approach)
- *Green solutions for solvents*

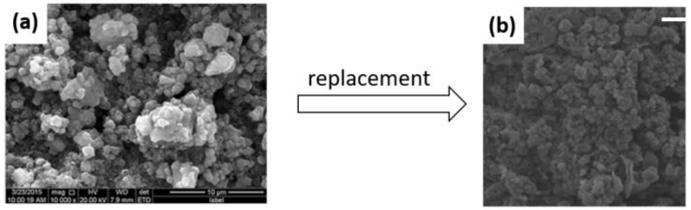
Binder candidate selection

- **Literature review** on binder materials either commercially available or novel, synthesized binder materials (polymers) for electrodes
- **Literature review** on solvent replacement/green alternatives/what processes are used or could be used in combination with greener solvents
- <u>Evaluation based on requirements</u>
  - Why PVDF?
    - What makes it the standard?
    - Which structural properties are needed?
  - Binder alternatives (commercial polymers)
  - Binder alternatives from novel synthetic approaches
- <u>Result – Binder candidates for PVDF replacement</u>
  - Commercially available polymer candidates
  - Design of new binder polymer (e.g. copolymer)
  - Green solvent candidates/processes in combination with green solvents

Electrode fabrication

<u>Electrode fabrication (slurry, casting, calendaring, etc.)</u>

- Electrode fabrication using standard PVDF binder
  - Standard solvent (=NMP)
  - Standard process (=slurry, casting, calendaring)
- Reference electrode for battery cell
- Electrode fabrication using commercial polymer candidates
  - Variation in formulation (e.g. binder content%)
  - Variation in solvent (e.g. H_2O, dry or wet)
  - Alternative polymer binders (commercial)
  - Variation in processing conditions (e.g. electrospinning, impregnation)
- Electrode fabrication using synthesized polymer candidates
  - Variant in formulation
  - Variation in solvent
  - Variation in polymer binder
  - Variation in processing conditions



a) PVDF + carbon black in batteries (scale bar = 10 um)
b) Fluorine-free replacement

Performance evaluation

- Characterization of electrode performance (T, PR, LNMO, conductivity, etc.)
- Performance evaluation of electrode in battery cell

Case Study #2

Aqueous Film-Forming Foams (AFFF)

Technology Focus

- Develop safe foams complying with MilSpec requirements by using new combinations of additives and surfactants

Research Objectives

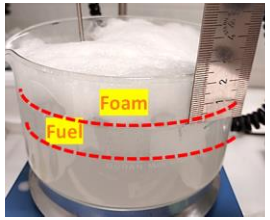
- Enhance firefighting properties of PFAS-free foaming formulations by the action of clay nanoparticles and water-soluble polymers
- Establish relationship between the fire extinguishing performance and the types of nanoparticles, polymers, and surfactants and produce environmentally safe foams

Progress Summary

- Various particle-polymer combinations identified that were compatible with surfactants and fire suppressing agents. Formulation suspensions were stable.
- Systematic study conducted on the effect of nozzle type
- Successful 1 ft^2 tests with 3% concentrate
- First 28 ft^2 test completed in October 2023

<u>PFAS-free Foam</u>

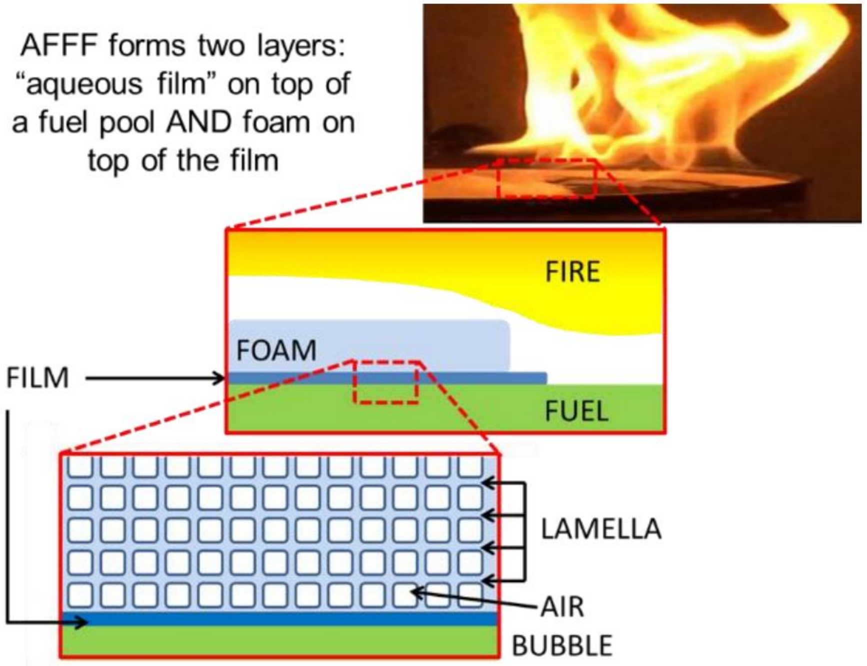
- Surfactants
- Polymers
- Nanoparticles
- Salts
- Stabilizers



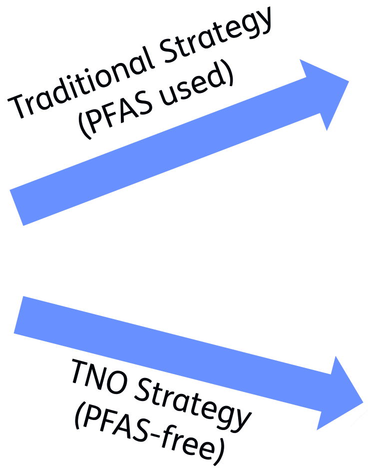
Foam Development

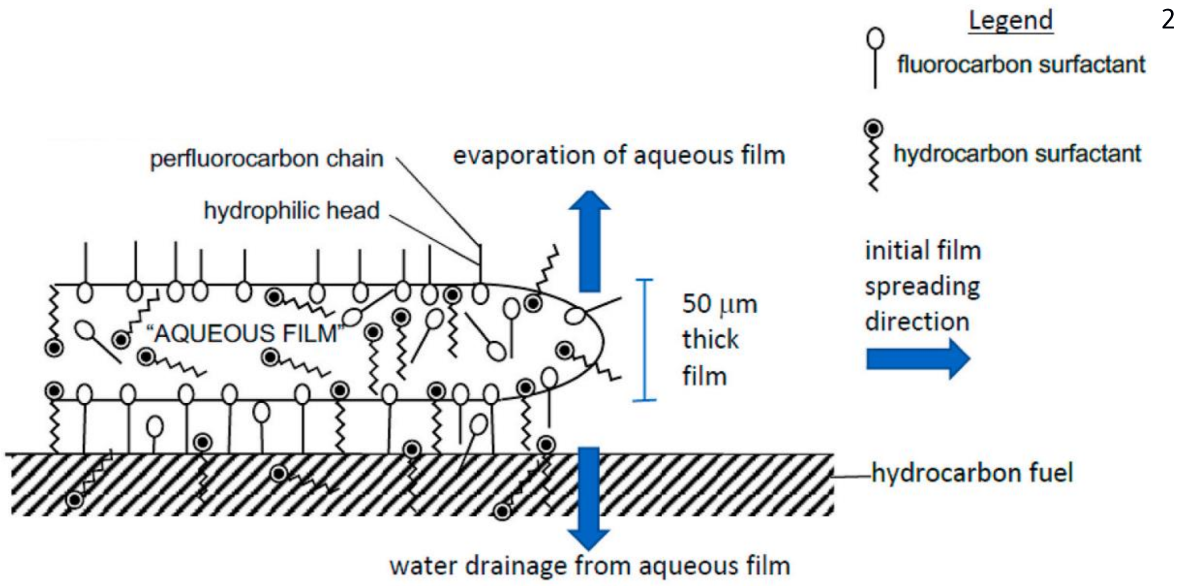
Aqueous Film-Forming Foams (AFFF)

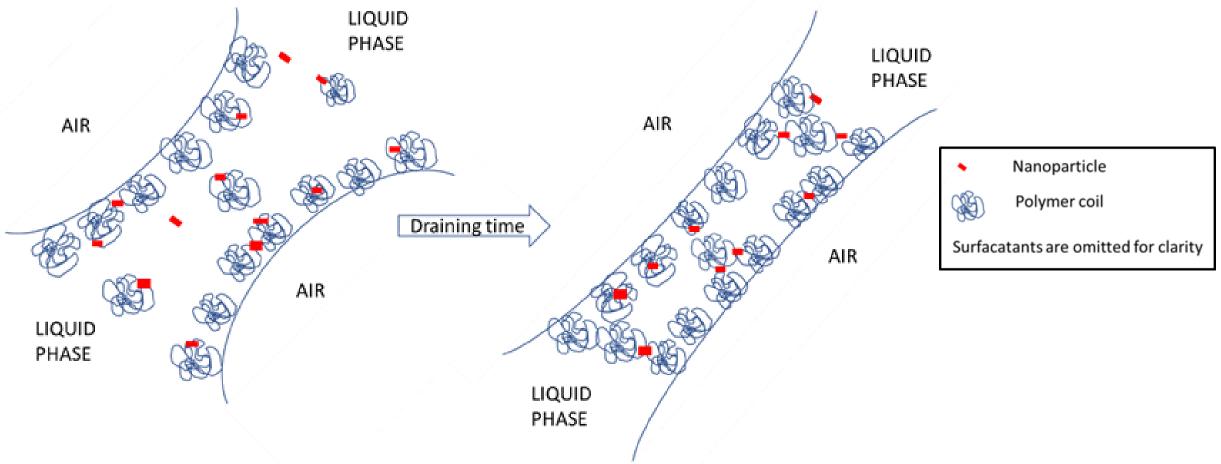
AFFF forms two layers: "aqueous film" on top of a fuel pool AND foam on top of the film



General AFFF concept







Synergistic action of polymers and nanoparticles trap water in polymer lamellae

1. Naval Research Laboratory, Environmentally-Friendly Surfactants for Foams with Low Fuel Permeability Needed for Effective Pool Fire Suppression, NRL/MR/6180--20-10,145
2. B. Dlugogorski, *Fire Safety Journal*, 120 (2021) 103288.

Fire-fighting tests at NRL (28 ft^2)

Jet Fuel A

Conclusions

- There are many R&D opportunities to improve semiconductor sustainability
- Replacing PFAS is motivated by economic, legal, and societal factors
- Identifying PFAS replacements is often very challenging due to their unique chemistry
- Clear requirements, product assessments, and formulation strategies are needed when developing alternatives
- PFAS replacements can range from a 1:1 solution to a complex formulation

THANK YOU FOR YOUR TIME

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