Fuel Cell Technologies Program Record	
Record #: 11015	**Date:** September 29, 2011
Title: Assessment of Perfluorinated Pollutants Associated with Fuel Cells	
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Item

Long-chain perfluorinated chemicals (PFCs) are used by some manufacturers as processing agents in the production of materials for polymer electrolyte membrane fuel cells. A 2006 agreement between the U.S. Environmental Protection Agency and the major manufacturers of long-chain PFCs, enacted due to concerns about the status of long-chain PFCs as bioaccumulative pollutants, is expected to result in elimination of these chemicals from production of fuel cell materials by 2015. While some PFCs may be generated through degradation of fuel cell materials, the short chain length of these PFCs makes them less likely to bioaccumulate.

Supporting Information

Background

Long-chain PFCs, including perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), are bioaccumulative persistent organic pollutants. PFCs have been demonstrated to have negative effects on laboratory animals and wildlife [1]. While significant negative effects have not been observed in the general human population, the long half-life of these chemicals in humans, and the potential for bioaccumulation, are cause for concern. Since the late 1990s, the U.S. Environmental Protection Agency (EPA) has been aware of the potential adverse impacts of PFCs, and has acted to minimize the impact of PFCs on human health and the environment [1,2].

Among PFCs, the eight-carbon chemicals PFOA and PFOS have received the most attention as pollutants, owing to their historically widespread use as processing agents and component materials in a variety of industrial and consumer product applications. Examples include the use of PFOA as a polymerization surfactant in production of polytetrafluoroethylene (PTFE) and related polymers, and the use of PFOS as an active component in oil, water, grease, and stain repellants for clothing, carpets, and upholstery. In 2000, EPA and the 3M Company reached an agreement in which 3M, the principal U.S. manufacturer of PFOS, would phase out PFOS production [3], a process that was completed by 2003 [1]. In 2006, EPA and eight major chemical companies launched the PFOA Stewardship Program, in which the eight major fluoropolymer and telomer manufacturers committed to reduce global facility emissions and product content of PFOA and related chemicals by 95% by 2010, and to work toward eliminating emissions and product content by 2015 [5].

As further research is performed on PFCs, further restrictions on usage and emissions are likely. EPA intends to propose actions in 2012 under the Toxic Substances Control Act to address the potential risks of long-chain PFCs [1]. These actions may lead to a ban on the manufacture, import, processing, and use of PFC pollutants. Such rules could address PFC-containing articles, as well as the chemicals themselves.

Regulation of the use of PFCs is also increasing internationally. The European Union has placed restrictions on the marketing and use of PFOS [5]. In 2009, PFOS was included in Annex B of the Stockholm Convention on persistent organic pollutants [6].

Regulatory attention to PFCs has focused on long-chain PFCs, since these compounds typically have longer half-lives in humans than shorter-chain PFCs. The EPA Long-Chain Perfluorinated Chemicals Action Plan examines PFCs with six or more carbons, specifically excluding PFCs with shorter chain lengths [1].

PFCs in Fuel Cells

The DOE Fuel Cell Technologies Program has identified two potential sources of long-chain PFC pollutants related to polymer electrolyte membrane fuel cells (PEMFCs): fluorinated engineering polymers, which are used as membrane mechanical support structures and blending agents, and perfluorosulfonic acids (PFSAs), which are used as electrolyte membranes and as a component of catalyst layers. The potential for release of long-chain PFCs via their use as processing agents in preparation of these materials, as well as through materials degradation, has been assessed by DOE through discussion with polymer and fuel cell material manufacturers, and through review of publicly available information.

Fluorinated polymers, such as polytetrafluoroethylene (PTFE), are widely used as mechanical support materials in PEMFCs due to their excellent mechanical properties and chemical stability. PFOA is used in PTFE synthesis, and some PFOA is retained in the resulting PTFE product. However, the PTFE fine powder used to produce fuel cell materials contains only trace levels of PFOA (<5 ppm). As part of the DuPont/EPA agreement [4], PFOA will be completely eliminated from PTFE produced by DuPont by 2015 [7].

Fluorinated polymers are also blended with ionomers in some PEMs. For instance, Arkema uses PVDF as a blended material in membranes for hydrogen PEMFCs and direct methanol fuel cells. Arkema uses ammonium perfluorononanoate (APFN) in production of PVDF, resulting in APFN levels of 80 – 110 ppm in the resulting PVDF as of 2006 [8]. Pursuant to Arkema's agreement with EPA [4], APFN should be eliminated by 2015.

PFSAs are widely used as ion conductors in PEMFCs. PFSAs contain a polymer backbone similar to PTFE, with sulfonated side chains to provide acid sites for ionic conductivity. As of 2009, DuPont does not use PFOA or PFOS in production of Nafion® [7], nor does 3M use PFOA, PFOS, or any related chemical in production of 3M ionomers [9]. It is unknown whether other PFSA suppliers use long-chain PFCs as processing agents [10].

The possibility that chemical degradation of PEMFC components could generate long-chain PFC pollutants has been considered, and determined to be unlikely. Analysis of cell degradation products by 3M indicated that $HO_2C(CF_2)_3SO_3H$ (Product A) was the only organic species of any size resulting from degradation of 3M ionomers, while similar testing with Nafion® revealed only $HO_2CCF(CF_3)\text{-}O\text{-}CF_2CF_2SO_3H$ (Product B) [9,11]. Similarly, a study by GM found that Product B was the primary organic degradation product of Nafion® in fuel cell testing [12], and a study by Case Western Reserve University found that Product B was the major organic reaction product from Fenton's degradation of Nafion® [13]. In all these cases, the primary organic degradation products corresponded to detached side chains, which contain fewer than six carbon atoms in typical PFSAs. Therefore, chemical degradation is not expected to produce the long-chain PFCs (containing six or more carbons) that are targeted by the Long-Chain PFCs Action Plan [1].

References

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