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Lessons Learned—Fluoride Exposure

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ABSTRACT: Laboratory workers are potentially exposed to a wide range of chemical hazards while performing experimental research. Moreover, unique combinations of chemicals can generate hazards that the individual chemical compounds would not produce. Thus, researchers may lack proper personal protective equipment to adequately protect themselves. A recent incident is examined in which a researcher suffered a painful hydrofluoric acid (HF) burn when working with a solution of lithium hexafluorophosphate ($LiPF_6$) dissolved in a mixture of dimethyl carbonate and ethylene carbonate. Under ambient conditions, $LiPF_6$ can produce HF, which by itself does not easily permeate nitrile gloves. However, the carbonate mixture rapidly permeates nitrile gloves. The mixture carried HF through the nitrile gloves allowing for rapid permeation. The compounding hazards led to nitrile gloves being inadequate protection for such an experiment. This Letter describes this incident and discusses how a proper risk assessment could prevent similar incidents from occurring.

KEYWORDS: *lithium hexafluorophosphate, hydrofluoric acid, fluoride, exposure, personal protective equipment, chemical compatibility lessons learned*

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■ WHAT HAPPENED?

A first-year postdoctoral scholar was working with lithium hexafluorophosphate ($LiPF_6$) as an electrolyte for battery development. The researcher was dispensing 1 mL aliquots of $LiPF_6$ dissolved in a dimethyl carbonate (DMC) and ethylene carbonate (EC) mixed solvent, under ambient conditions. During the procedure, the researcher pressed the tip of the pipet onto their left index finger while wearing disposable nitrile gloves as protection. The researcher experienced instant pain that rapidly increased in severity. Recalling that alkyl carbonate solutions of $LiPF_6$ may generate hydrofluoric acid (HF), the researcher immediately flushed their hand with copious amounts of water before applying calcium gluconate gel to the affected area. The researcher called the research safety office and then proceeded to the hospital emergency room for additional treatment. Fortunately, no permanent scaring occurred. At the time of the incident, the researcher was wearing a lab coat and splash goggles in addition to disposable nitrile gloves.

■ WHAT WAS THE CAUSE?

Disposable nitrile gloves are permeable to dimethyl carbonate which enabled the dissolved lithium hexafluorophosphate to penetrate the skin. Furthermore, the mixture can generate HF, which also permeates nitrile gloves. $LiPF_6$ is relatively stable under dry inert conditions; however, it degrades upon exposure to traces of water, moisture, or alcohols. It has been proposed that the reaction starts with the dissociation of $LiPF_6$, reaction 1,[1−3] to form lithium fluoride (LiF) and phosphorus pentafluoride (PF_5):

$$LiPF_6 \rightleftarrows LiF + PF_5 \quad (1)$$

Reaction 1 is negligible under ambient conditions; however, when $LiPF_6$ is dissolved in battery electrolytes, such as EC and DMC, PF_5 is stabilized by coordination to the solvent molecules, shifting the equilibrium to the product side favoring generation of PF_5. Thus, any trace water molecules in the solution can then react with the PF_5 to form phosphoryl fluoride (POF_3) and HF (reaction 2):[1−3]

$$PF_5 + H_2O \rightarrow POF_3 + 2HF \quad (2)$$

As HF is absorbed into the bloodstream, it interferes with nerve functions. Initial contact may not be painful, but adsorbed fluoride salts and hydrofluoric acid can cause severe pain and systemic toxicity.

The solvent-dependent mechanism of HF formation and its toxicology, compounded by an inadequate PPE choice, comprise the immediate causes for the incident. The root causes included a lack of a standard operating procedure (SOP) specifying appropriate personal protective equipment

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(PPE) when using fluoride salts and a lack of a risk assessment for the specific experiment. Thus, corrective actions were necessary to prevent other incidents of this kind.[4]

■ WHAT CORRECTIVE ACTIONS WERE TAKEN?

After the incident occurred and the researcher received proper treatment, several corrective actions were performed by the research group in partnership with the Northwestern University Research Safety Office:

1. The incident as well as the specific hazards of hydrofluoric acid and fluoride salts were discussed with the laboratory group members.
2. A risk assessment was conducted in order to identify all hazards and determine how to properly control, reduce, or eliminate the risks.
3. The risk assessment included a review of the safety data sheet (SDS) of the chemicals involved, and it was noted that the SDS for the individual chemicals[5−8] recommended specific types of gloves, but the SDS for commercial $LiPF_6$ solutions in carbonate solvents did not recommend any specific type of glove.[9]
4. Based on the risk assessment, proper procedures for handling $LiPF_6$ solutions were developed into an SOP.
5. PPE was reviewed by the Research Safety Office, and researchers were trained to use the combined layered protection of two chemical-resistant gloves when working with fluoride salts, hydrofluoric acid, and other corrosive chemicals. The two gloves chosen were a disposable nitrile/neoprene glove over a Silvershield glove. The Silvershield glove was selected for the use of these $LiPF_6$ solutions due to the glove's high breakthrough times for a broad range of organic carbonates, esters, ketones, and dilute HF solutions,[10] in order to protect against dermal contact during incidental splashes and spills. However, due to the fragile nature of SilverShield it is recommended to wear a long nitrile/neoprene glove over the SilverShield glove to protect it from tears and punctures, tucking excess gloves under the lab coat sleeve (Figure 1).

Figure 1. Demonstration of proper PPE protection of a SilverShield glove layered under a long nitrile/neoprene glove for the laboratory's use of $LiPF_6$ solutions in carbonate solvents.

■ HOW CAN INCIDENTS LIKE THIS BE PREVENTED?

1. Conduct a risk assessment before starting new experiments utilizing fluoride salts, hexafluorophosphates, or other compounds that may generate hydrofluoric acid by
   a. consulting the safety data sheet (SDS) of ALL chemical reactants, solvents, and products involved in the experiments to identify the chemical hazards;
   b. considering possible side reactions, such as solvent-induced decomposition pathways, to identify additional chemical hazards and consulting appropriate SDS for those chemicals;
   c. choosing the correct protective glove type[10,11] as part of appropriate PPE, equipment, and engineering controls based on these chemical hazards (glove type should be chosen not only for hazardous reagents and products in a reaction, but also for the associated solvent that may allow permeation, and subsequent skin exposure, of hazardous chemicals through the glove);
   d. consulting your EH&S department, or the glove's manufacturer, if identifying the appropriate glove for a particular chemical or chemical reaction is unclear (the chemical's SDS may not specify a glove type for a particular chemical mixture; breakthrough times of chemical mixtures, particularly in solute−solvent combinations, are complicated[12] and should be assessed with the help of health and safety professionals as well as the glove manufacturer);
   e. developing SOPs (see SOP for HF[13] and SOP template[14]) for all experiments to list the proper materials, protection, and procedures needed;
   f. training research group members on the SOPs before they conduct experiments.
2. Ensure that calcium gluconate gel is available in the laboratory when experiments are conducted with hydrofluoric acid or fluoride salts, and check the expiration date since it has a limited shelf life.
3. Ensure that the hazards of hydrofluoric acid and fluoride salts are understood by everyone that works with them. Hydrofluoric acid is highly corrosive and causes severe skin burns, eye damage, and tissue death. Once adsorbed it can cause bone damage and act as an acute poison leading to cardiac arrest.

■ QUICK ACTION TIPS AND HF EXPOSURE EMERGENCY PROTOCOL

This incident highlights the need to consider reaction products, byproducts, and side products, in addition to unique solvent effects, when assessing toxicity risks and developing effective PPE requirements.

If there is skin exposure to hydrofluoric acid, do the following:[15]

1. HF exposure requires immediate specific and specialized medical treatment.
2. Rinse the affected area with copious amounts of cool water for 5 min to remove surface HF residues.
3. Apply liberal amounts of calcium gluconate gel on the burned area and continuously massage into the skin. (Note that the medical efficacy of 2.5% calcium gluconate gel has been experimentally evaluated.[16])
4. If the victim cannot wash the area and apply the gel themselves, the person assisting should wear appropriate HF-protective gloves (e.g., neoprene rubber).
5. If HF has penetrated underneath fingernails, the gel should be liberally applied over and around the area and continually massaged for 15 min.
6. Seek immediate medical attention.

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7. Reapply gel and massage into the affected area every 15 min until medical assistance is obtained.
8. Report the incident to your supervisor.
9. Report the incident to the institution EH&S department or Research Safety Office.

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Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Lux, S. F.; Lucas, I. T.; Pollak, E.; Passerini, S.; Winter, M.; Kostecki, R. The mechanism of HF formation in $LiPF_6$ based organic carbonate electrolytes. *Electrochem. Commun.* **2012**, *14* (1), 47−50.

(2) Tasaki, K.; Kanda, K.; Nakamura, S.; Ue, M. Decomposition of $LiPF_6$ and Stability of PF_5 in Li-Ion Battery Electrolytes. *J. Electrochem. Soc.* **2003**, *150* (12), A1628.

(3) Stich, M.; Göttlinger, M.; Kurniawan, M.; Schmidt, U.; Bund, A. Hydrolysis of $LiPF_6$ in Carbonate-Based Electrolytes for Lithium-Ion Batteries and in Aqueous Media. *J. Phys. Chem. C* **2018**, *122*, 8836−8842.

(4) Use Lessons Learned to improve the safety program in your lab. https://cls.ucla.edu/lessons-learned (accessed December 20, 2019).

(5) Sigma-Aldrich Safety Data Sheet: Lithium hexafluorophosphate. https://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=450227&brand=ALDRICH&PageToGoToURL=https%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Faldrich%2F450227%3Flang%3Den (accessed December 20, 2019).

(6) Sigma-Aldrich Safety Data Sheet: Hydrofluoric acid. https://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=695068&brand=SIGALD&PageToGoToURL=https%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Fsigald%2F695068%3Flang%3Den (accessed December 20, 2019).

(7) Sigma-Aldrich Safety Data Sheet: Dimethyl carbonate. https://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=517127&brand=SIAL&PageToGoToURL=https%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Fsial%2F517127%3Flang%3Den (accessed December 20, 2019).

(8) Sigma-Aldrich Safety Data Sheet: Ethylene carbonate. https://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=E26258&brand=ALDRICH&PageToGoToURL=https%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fproduct%2Faldrich%2Fe26258%3Flang%3Den (accessed December 20, 2019).

(9) Sigma-Aldrich Safety Data Sheet: Lithium hexafluorophosphate solution. https://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=746711&brand=ALDRICH&PageToGoToURL=https%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fsearch%3Fterm%3Dlithium%2Bhexafluorophosphate%26interface%3DAll%26N%3D0%26mode%3Dmatch%2520partialmax%26lang%3Den%26region%3DUS%26focus%3Dproduct (accessed January 7, 2019).

(10) VWR Hand Protection Chemical Resistance Guide. https://eta-safety.lbl.gov/sites/default/files/VWR%20Chemical%20Resistance%20Gloves%20Chart.pdf (accessed December 20, 2019).

(11) Glove Selection Guide | Environment, Health & Safety. https://ehs.berkeley.edu/workplace-safety/glove-selection-guide#comparison (accessed December 20, 2019).

(12) Watkinson, A. C.; Brain, K. R.; Walters, K. A.; Hadgraft, J. Investigation of relative rates of solvent and solute penetration through protective glove materials. *Pestic. Sci.* **1993**, *39* (3), 251−256.

(13) Harvard University, Guidelines for the Safe Use of Hydrofluoric Acid. https://chemistry.harvard.edu/files/chemistry/files/safe_use_of_hf_0.pdf (accessed December 20, 2019).

(14) Standard Operating Procedure, Research Safety, Northwestern University. https://cpb-us-e1.wpmucdn.com/sites.northwestern.edu/dist/b/2789/files/2019/09/sop_template.pdf (accessed December 20, 2019).

(15) Recommended Medical Treatment for Hydrofluoric Acid Exposure, Honeywell. https://sms.asu.edu/sites/default/files/honeywell-hf-medical-brochure-2012-final.pdf (accessed December 20, 2019).

(16) Roblin, I.; Urban, M.; Flicoteau, D.; Martin, C.; Pradeau, D. Topical treatment of experimental hydrofluoric acid skin burns by 2.5% calcium gluconate. *J. Burn Care Res.* **2006**, *27* (6), 889−894.