

Acid/Base Buffering Capacity in Molten Fluoride Salts

Haley Williams haley_williams@berkeley.edu University of California - Berkeley

Introduction

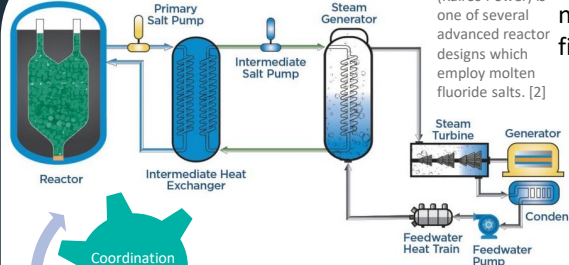
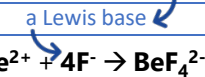


Fig 1. KP-FHR (Kairos Power) is one of several advanced reactor designs which employ molten fluoride salts. [2]

Molten salts may be used for the pyroprocessing of nuclear waste or as coolants and/or fuel carriers in fission and fusion reactors. [1]

fluorobasicity
 $pF = -\log(a_{F^-})$



Acid/base behavior is related to:

- composition, which may be dynamic
- the degree of dissociation of the melt, coordination numbers of cations
- the chemical potential which fixes the ratio of valence states of a given cation (redox potential) [3]

Methods

Ab-initio molecular dynamics simulations were used to study the short range and medium range structure of $2KF-NaF$, $2LiF-BeF_2$, and $3LiF-AlF_3$ with and without Cr addition. [4]

~100 atom cell each, melts of various pF
 the structural metal favored to oxidize to a fluoride

- Charge neutrality maintained upon Cr addition by removing cations
- Thermostat 700°C to reproduce operating conditions of the Molten Salt Reactor Experiment of the 1960s

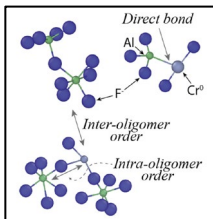


Fig 2. $3LiF-AlF_3$ with Cr^0 indicating order within and between oligomers. [4]

Short range: first nearest neighbors, coordination of cations by F⁻

Medium range: second nearest neighbors and shared connections between coordination shells, oligomeric organization at longer length scales

Research Highlights

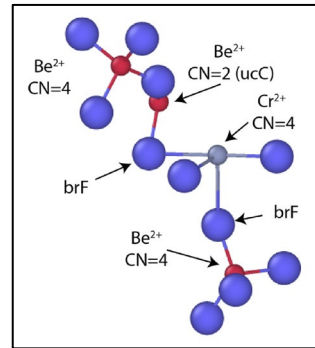


Fig 3. $2LiF-BeF_2$ with Cr^{2+} . Indicates bridging fluorides (brF) and under-coordinated cation centers (ucC) where the coordination number (CN) of Be^{2+} is less than its nominal CN of 4. [4]

This work challenges the previous understanding of fluorobasicity's role in corrosion.

➔ Cr can incorporate into and be solvated within the oligomer structure of the melt. It does not require a more basic melt (containing more dissociated F⁻ (dsF)) to solvate chromium.

This work introduces the concept of buffering capacity for molten fluoride salts.

➔ Buffering capacity is the ability to produce dsF (maintain pF) in response to consumption of dsF (during corrosion, in the event of Cr solvation).

The state in which F⁻ was found in each melt (dissociated, bridging, or terminal) was examined. Fluoride in $2KF-NaF$ is completely dissociated.

For the melts which did form associates, two types of acid/base reactions may occur: 1) change in monomer CN, or 2) association/dissociation of oligomers.

	2KF-NaF	Be-F in 2LiF-BeF ₂	Al-F in 3LiF-AlF ₃
fluorobasicity	100 %	13(1) % of F ⁻ 0.51(4) per Be ²⁺	15(1) % of F ⁻ 0.91(5) per Al ³⁺
acid-base buffering capacity		0.42(3) per Be ²⁺	0.26(4) per Al ³⁺
		0.100(5) per Be ²⁺	0.59(3) per Al ³⁺
		90% CN = 4 10% CN = 3	41% CN = 6 52% CN = 5 7% CN = 4

Results

brF & ucC are used to analyze acidic behavior:
 ➔ brF indicate a higher degree of polymerization
 ➔ ucC are acidic species

If defining pF by counting basic ions (dsF), $3LiF-AlF_3$ is more basic than $2LiF-BeF_2$. Considering pF in terms of acidic character (brF + ucC), $3LiF-AlF_3$ is more acidic.

Discussion & Conclusion

High brF concentration and/or a capacity for undercoordination (multiple possible CNs) may be considered as **acid/base buffering capacity**. This means that the melt is able to produce dsF in response to consumption of dsF by solvation of a Cr cation.

The contribution to acidity (brF vs ucC) depends on the melt composition, as well. Both degree of polymerization and degree of association must be considered. Thus, acidic behavior should be studied in addition to basicity.

- Next steps: Experimental validation to quantify how chromium ions behave (measuring diffusivity of Cr^{2+} and Cr^{3+}) in melts of varying pF is currently in progress.

Acknowledgements & References

Advisor: Raluca O. Scarlat, Funding: FUTURE EFRC, NEUP 21-24563

- [1] S. Delpech, et al. "Molten salts for nuclear applications," In *Molten Salts Chemistry*, 2013. [2] From "Kairos Power: DOE-NE IRP to Nuclear Startup", DOE NEUP. [3] D. Olander, "Redox condition in molten fluoride salts: definition and control," *J. Nuc. Mat.*, 2002. [4] N. Winner, et al. "Ab-initio simulation studies of chromium solvation in molten fluoride salts." *J. Mol. Liq.*, 2021.



Read more in the EFRC newsletter!