Redox Potential of Novel Electrochemical Buffers Useful for Corrosion Prevention in Molten Fluorides

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Advanced High-Temperature Reactors (AHTRs) that have improved safety features and more efficient energy conversion systems constitute a new generation of nuclear power reactors. A molten-fluoride cooled version of the High Temperature Gas-cooled Reactor (HTGR) offers the benefits of high thermodynamic efficiency, additional fission product containment, and several enhanced safety features (low-pressure operations, passive cooling).

The primary technical hurdle for use of molten salts at higher temperatures (~1000°C) is materials performance. Understanding the role of corrosion and preventing materials degradation is the key requirement. During the Molten Salt Reactor Program it was established that a controlled, mildly reducing environment improves the compatibility of the container with a molten salt. For molten salt fuels this was established using the U(IV/III) soluble redox couple as an electrochemical buffer. For actinide-free molten salt coolants operating at very high temperatures in an AHTR, we propose a new set of redox buffers: Tm(III/II), Sm(III/II), Yb(III/II), V(III/II) and Eu(III/II). Work in related chloride and fluoride salts (Table 1) suggests that these redox-sensitive rare earths (and vanadium) are the most useful candidates for preventing container corrosion. Our present interest is in "FLiNaK" LiF-NaF-KF (46.5-11.5-42 mol %) and LiF-MgF_2 (66-34 mol %) as prototypical coolant salts. The experimentally determined standard redox potentials of these new electrochemical buffers are compared with the literature on analogous chloride systems, and related fluoride systems.

Redox couples	Standard reduction potential (V)	
	LiCl-KCl at 450°C	2LiF-BeF_2 at 700°C
Li(I) – Li(0)	-3.62	-2.56
Mg(II) – Mg(0)	-2.88	–
Be(II) – Be(0)	–	-1.765
Zr(IV) – Zr(0)	-2.13	-1.355
Sm(III) – Sm(II)	-2.035	–
Yb(III) – Yb(II)	-1.68	–
U(IV) – U(III)	-1.55	-1.045
V(III) – V(II)	-1.07	–
Eu(III) – Eu(II)	-0.86	–
Reference couples		
HF – ½ H_2	–	0
½ Cl_2 – Cl^-	0	–

Table 1. Electrochemical measurement of redox couples in chlorides and fluorides (from references *[1-5]*).

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