Supporting Information

Probing the Ionic Structure of FLiNaK-ZrF₄ Salt Mixtures by

Solid-State NMR

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- Figure S1. ¹⁹F solid-state MAS NMR spectra of different ZrF₄ components in FLiNaK-ZrF₄ (0≤X_{ZrF4}≤13.6 mol%) systems at room temperature. MAS spin rate in these experiments was set to 15 kHz. Spinning sidebands were marked with asterisks. (-300≤δ≤50ppm)
- Figure S2. XRD spectra of FLiNaK and FLiNaK-ZrF₄ (3.56 mol%) salt at room temperature.
- **Figure S3.** Integrate of the ²³Na NMR signal of NaF in FLiNaK-ZrF₄ ($0 \le X_{ZrF4} \le 13.6 \text{ mol}\%$) systems versus the molar fraction of ZrF₄ components.
- **Figure S4.** Integrate of the ⁷Li NMR signal of LiF in FLiNaK-ZrF₄ ($0 \le X_{ZrF4} \le 13.6$ mol%) systems versus the molar fraction of ZrF₄ components.
- Figure S5. ¹⁹F solid-state MAS NMR spectra of different ZrF_4 components in FLiNaK- ZrF_4 ($0 \le X_{ZrF4} \le 13.6 \text{ mol}\%$) systems at room temperature. MAS spin rate in these experiments was set to 15 kHz. Spinning sidebands were marked with asterisks.
- Figure S6. ¹⁹F solid-state MAS NMR spectra of different ZrF_4 components in FLiNaK-ZrF₄ ($0 \le X_{ZrF4} \le 18.3 \text{ mol}\%$) systems at room temperature. MAS spin rate in these experiments was set to 15 kHz.
- **Table S1.** The component analysis of LiF, NaF and KF in FLiNaK eutectic salt.
- **Table S2.** The number of kinds of ions and the ratio of $n(F^{-})$ to $n(Zr^{4+})$ in FLiNaK-ZrF₄ ($0 \le X_{ZrF4} \le 18.3 \text{ mol}\%$) systems.
- **Table S3.** The assignment of chemical shift in ¹⁹F solid-state MAS NMR spectra for
different ZrF₄-based systems.

Figure S1. ¹⁹F solid-state MAS NMR spectra of different ZrF₄ components in FLiNaK-ZrF₄ (0≤X_{ZrF4}≤13.6 mol%) systems at room temperature. MAS spin rate in these experiments was set to 15 kHz. Spinning sidebands were marked with asterisks. (-300≤δ≤50ppm)



Figure S2. XRD spectra of FLiNaK and FLiNaK-ZrF₄ (3.56 mol%) salt at room temperature.



Figure S3. Integrate of the ²³Na NMR signal of NaF in FLiNaK-ZrF₄ ($0 \le X_{ZrF4} \le 13.6 \text{ mol}\%$) systems versus the molar fraction of ZrF₄ components.



Figure S4. Integrate of the ⁷Li NMR signal of LiF in FLiNaK-ZrF₄ ($0 \le X_{ZrF4} \le 13.6$ mol%) systems versus the molar fraction of ZrF₄ components.



Figure S5. ¹⁹F solid-state MAS NMR spectra of different ZrF₄ components in FLiNaK-ZrF₄ (0≤X_{ZrF4}≤13.6 mol%) systems at room temperature. MAS spin rate in these experiments was set to 15 kHz. Spinning sidebands were marked with asterisks.



Figure S6. ¹⁹F solid-state MAS NMR spectra of different ZrF_4 components in FLiNaK-ZrF₄ ($0 \le X_{ZrF4} \le 18.3 \text{ mol}\%$) systems at room temperature. MAS spin rate in these experiments was set to 15 kHz. Spinning sidebands were marked with asterisks.



		m(Li)	m(Na)	m(K)	n(Li)	n(Na)	n(K)
		(mg)	(mg)	(mg)	(mol%)	(mol%)	(mol%)
	1	31.67	25.85	162.1	46.41	11.44	42.16
Entry	2	32.27	26.61	172.9	45.46	11.32	43.22
	3	35.31	27.74	186.3	46.00	10.91	43.09
Average		\	\	\	45.95	11.22	42.83
RSD(%)		\	\	\	1.04	2.45	1.35

Table S1. The component analysis of LiF, NaF and KF in FLiNaK eutectic salt.

n(ZrF ₄)	n(Li ⁺)	n(Na ⁺)	n(K ⁺)	n(F⁻)	$n(Zr^{4+})$	$n(E^{-})/n(Z_{r}^{4+})$
(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	$n(F)/n(Zr^{+})$
0	46.5	11.5	42	100	0	/
0.33	46.35	11.46	41.9	101	0.33	306
1.02	46.03	11.38	41.6	103	1.02	101
1.69	45.71	11.31	41.3	105	1.69	62
2.38	45.39	11.23	41.0	107	2.38	45
3.56	44.84	11.09	40.5	111	3.56	31
5.81	43.80	10.83	39.6	117	5.81	20
7.98	42.79	10.58	38.7	124	7.98	15.5
9.99	41.86	10.35	37.8	130	9.99	13
12.2	40.83	10.10	36.9	137	12.2	11
13.6	40.16	9.93	36.3	141	13.6	10.3
15.2	39.45	9.76	35.6	146	15.2	9.6
16.3	38.94	9.63	35.2	149	16.3	9.2
18.3	38.01	9.40	34.3	155	18.3	8.5

Table S2. The number of kinds of ions and the ratio of $n(F^{-})$ to $n(Zr^{4+})$ in FLiNaK-ZrF₄ ($0 \le X_{ZrF4} \le 18.3 \text{ mol}\%$) systems.

System	Chmical Shift	Assignment	Reference Chmical Shift	
System	$(\delta_{solid})/ppm$	Compounds	$(\delta_{solid})/ppm$	
	-35.0		-34.81	
	-36.9 K ₃ ZrF ₇		-36.51	
FLiNaK-ZrF ₄	-37.8		-37.11	
(0≤X _{ZrF4} ≤13.6 mol%)	-132.9	KF	-132.9 ²	
	-224.6	NaF	-224.6 ²	
	-205.4	LiF	-205.4^{2}	

 Table S3. The assignment of chemical shift in ¹⁹F solid-state MAS NMR spectra for different ZrF4-based systems.

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