## **Supporting Information**

## Probing the Ionic Structure of FLiNaK-ZrF<sub>4</sub> Salt Mixtures by

## Solid-State NMR

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- Figure S1. <sup>19</sup>F solid-state MAS NMR spectra of different ZrF<sub>4</sub> components in FLiNaK-ZrF<sub>4</sub> (0≤X<sub>ZrF4</sub>≤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-ZrF<sub>4</sub> (3.56 mol%) salt at room temperature.
- **Figure S3.** Integrate of the <sup>23</sup>Na NMR signal of NaF in FLiNaK-ZrF<sub>4</sub> ( $0 \le X_{ZrF4} \le 13.6 \text{ mol}\%$ ) systems versus the molar fraction of ZrF<sub>4</sub> components.
- **Figure S4.** Integrate of the <sup>7</sup>Li NMR signal of LiF in FLiNaK-ZrF<sub>4</sub> ( $0 \le X_{ZrF4} \le 13.6$  mol%) systems versus the molar fraction of ZrF<sub>4</sub> components.
- Figure S5. <sup>19</sup>F 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. <sup>19</sup>F solid-state MAS NMR spectra of different  $ZrF_4$  components in FLiNaK-ZrF<sub>4</sub> ( $0 \le X_{ZrF4} \le 18.3 \text{ mol}\%$ ) 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-ZrF<sub>4</sub> ( $0 \le X_{ZrF4} \le 18.3 \text{ mol}\%$ ) systems.
- **Table S3.** The assignment of chemical shift in <sup>19</sup>F solid-state MAS NMR spectra for<br/>different ZrF<sub>4</sub>-based systems.

**Figure S1.** <sup>19</sup>F solid-state MAS NMR spectra of different ZrF<sub>4</sub> components in FLiNaK-ZrF<sub>4</sub> (0≤X<sub>ZrF4</sub>≤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-ZrF<sub>4</sub> (3.56 mol%) salt at room temperature.



**Figure S3.** Integrate of the <sup>23</sup>Na NMR signal of NaF in FLiNaK-ZrF<sub>4</sub> ( $0 \le X_{ZrF4} \le 13.6 \text{ mol}\%$ ) systems versus the molar fraction of ZrF<sub>4</sub> components.



**Figure S4.** Integrate of the <sup>7</sup>Li NMR signal of LiF in FLiNaK-ZrF<sub>4</sub> ( $0 \le X_{ZrF4} \le 13.6$  mol%) systems versus the molar fraction of ZrF<sub>4</sub> components.



Figure S5. <sup>19</sup>F solid-state MAS NMR spectra of different ZrF₄ components in FLiNaK-ZrF₄ (0≤X<sub>ZrF4</sub>≤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. <sup>19</sup>F solid-state MAS NMR spectra of different  $ZrF_4$  components in FLiNaK-ZrF<sub>4</sub> ( $0 \le X_{ZrF4} \le 18.3 \text{ mol}\%$ ) 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 <sub>4</sub> )	n(Li <sup>+</sup> )	n(Na <sup>+</sup> )	n(K <sup>+</sup> )	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-ZrF<sub>4</sub> ( $0 \le X_{ZrF4} \le 18.3 \text{ mol}\%$ ) systems.

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

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

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2 Y. Y. Liu, R. S. Lan, C. W. Dong, K. Wang, X. B. Fu, H. T Liu, Y. Qian, J. Q. Wang, J. Phys. Chem. C, 2021, 125, 8, 4704–4709.