Electronic Supplementary Information

Fluorine-free "solvent-in-Salt" sodium battery electrolytes: Solvation structure and dynamics

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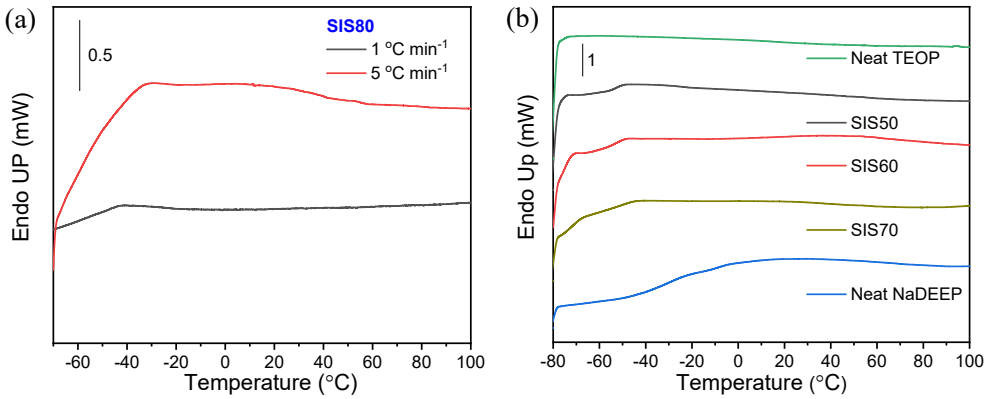

Figure S1. DSC traces of (a) SIS80 from -80 to 100 °C at 1 and 5 °C·min^{-1}, and (b) the NaDEEP salt, the TEOP solvent, and selected SIS*XX* electrolytes from -80 to 100 °C at 5 °C·min^{-1}.

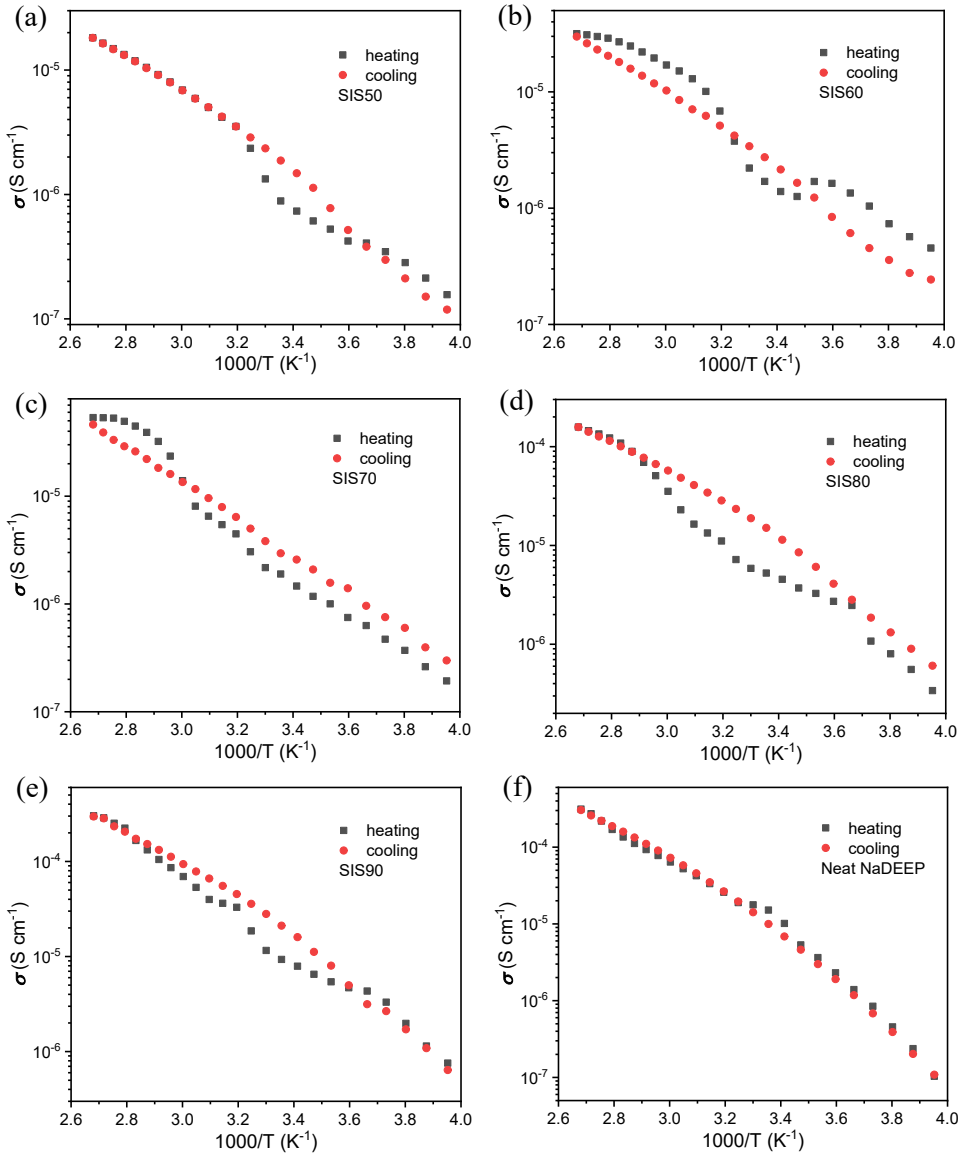

Figure S2. Ionic conductivities for (a-e) the SIS*XX* electrolytes and (f) NaDEEP as a function of temperature.

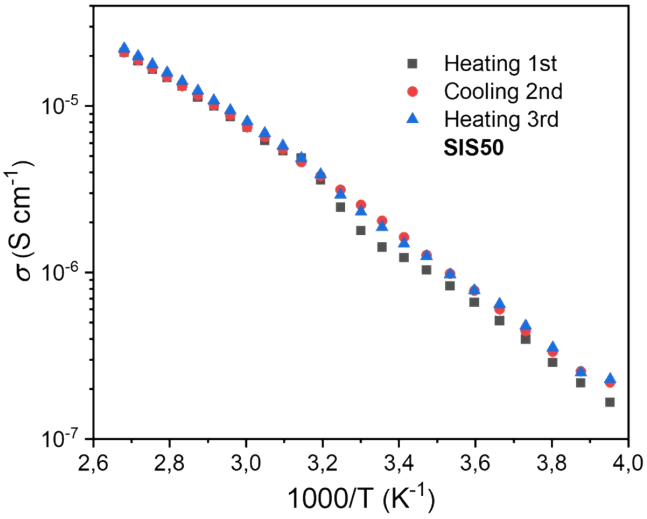

Figure S3. Ionic conductivities for the SIS50 electrolyte during heating-cooling-heating cycle.

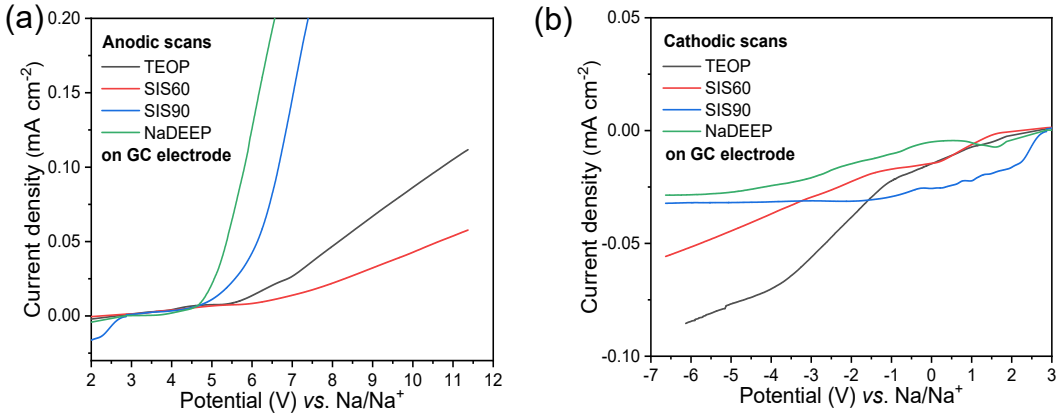

Figure S4. Anodic (a) and cathodic (d) LSV scans of TEOP solvent, SIS60, SIS90 and NaDEEP salt using a GC WE.

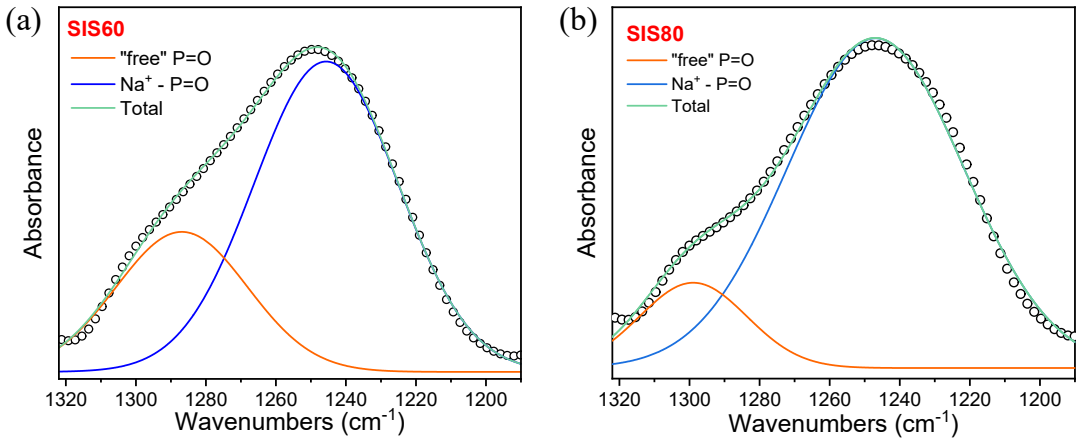

Figure S5. Deconvolution the P=O stretching vibrational mode for the SIS60 and SIS80 electrolytes.

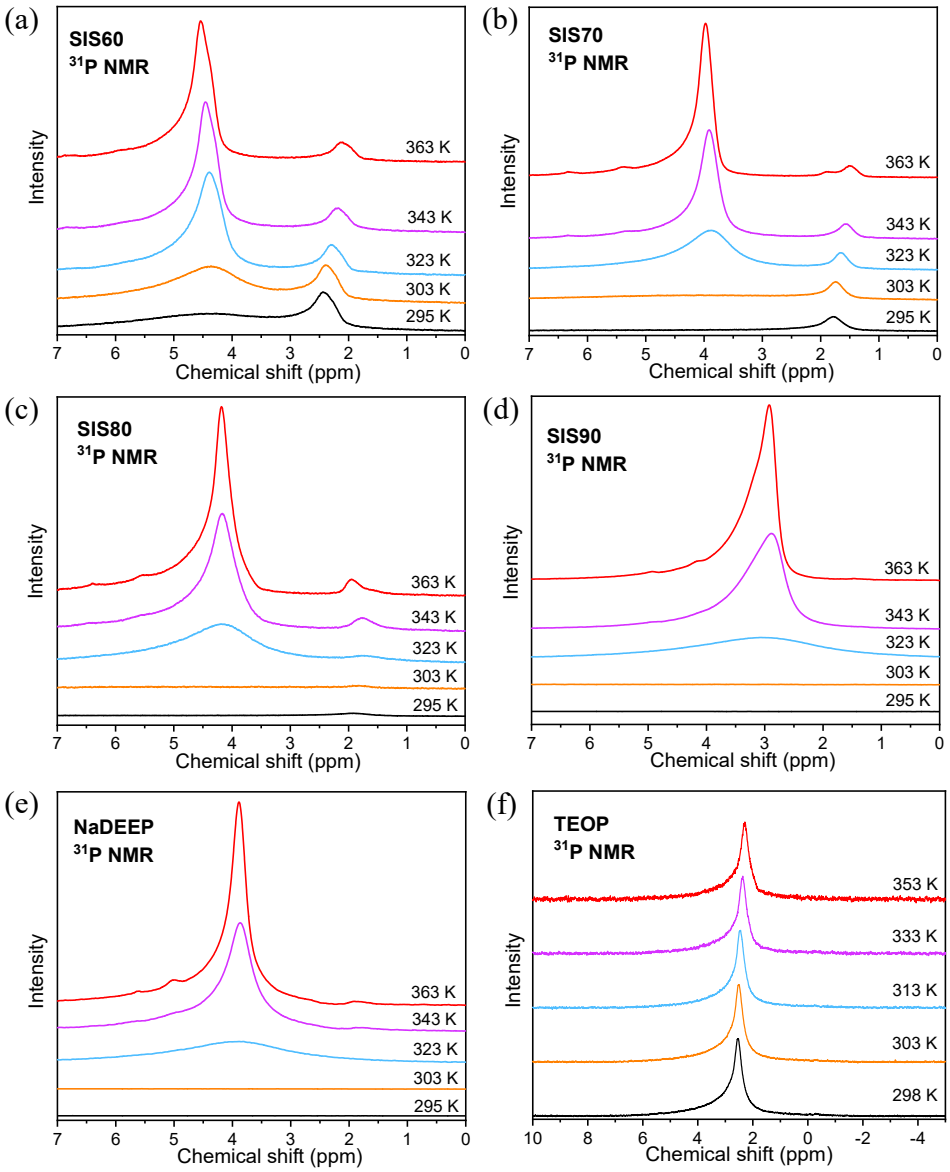

Figure S6. ^{31}P NMR spectra of (e) the NaDEEP salt, (f) the TEOP solvent, and (a-d) the SIS*XX* electrolytes.

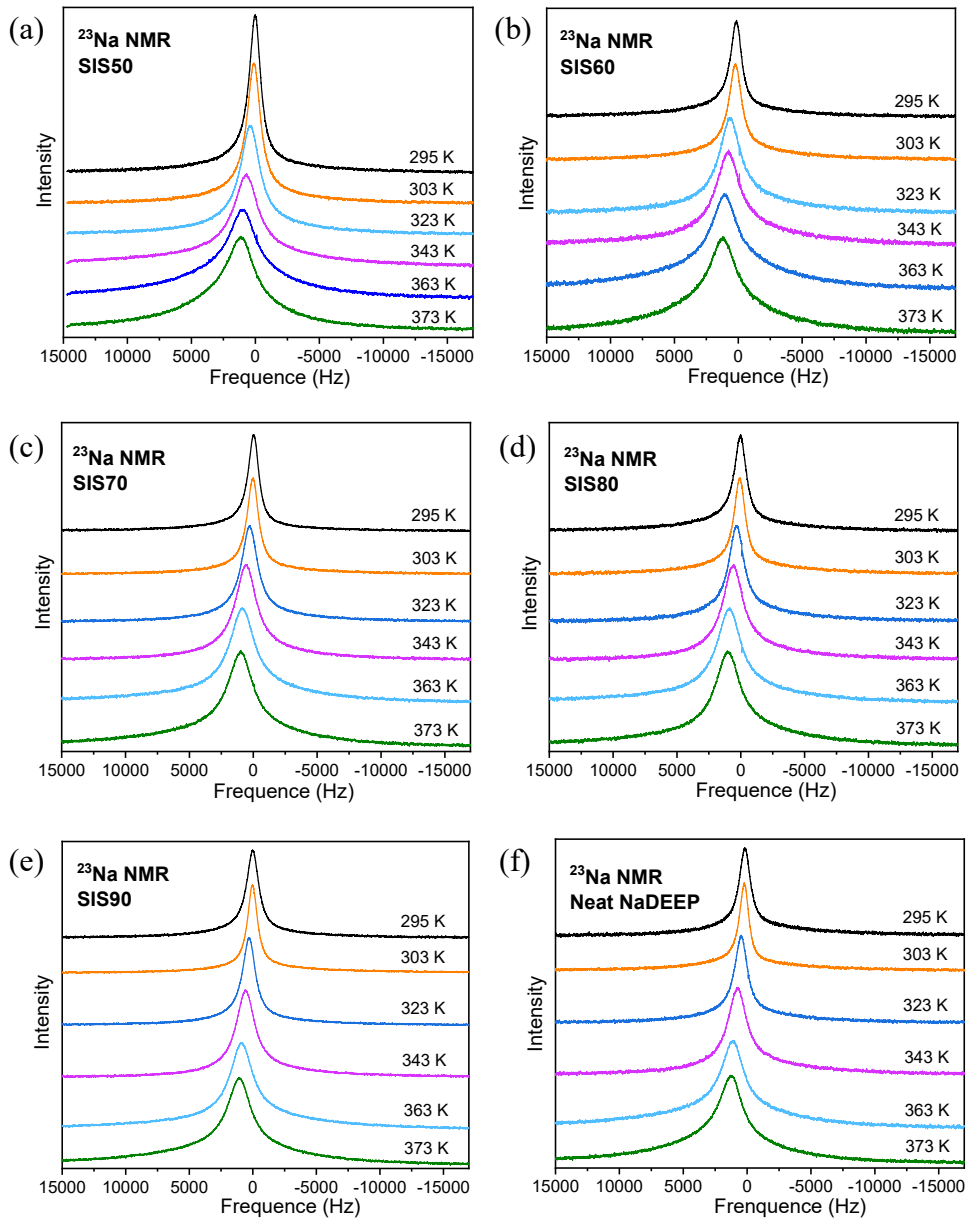

Figure S7. ^{23}Na NMR spectra of (f) the NaDEEP salt and (a-e) the SIS*XX* electrolytes.

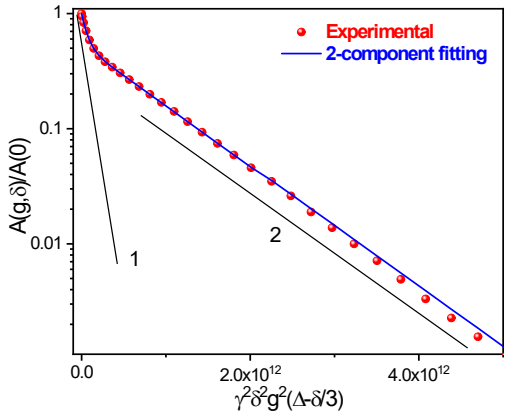

Figure S8. Experimental ^{1}H diffusion decay at 303 K and a two-component fitting for the SIS50 electrolyte.

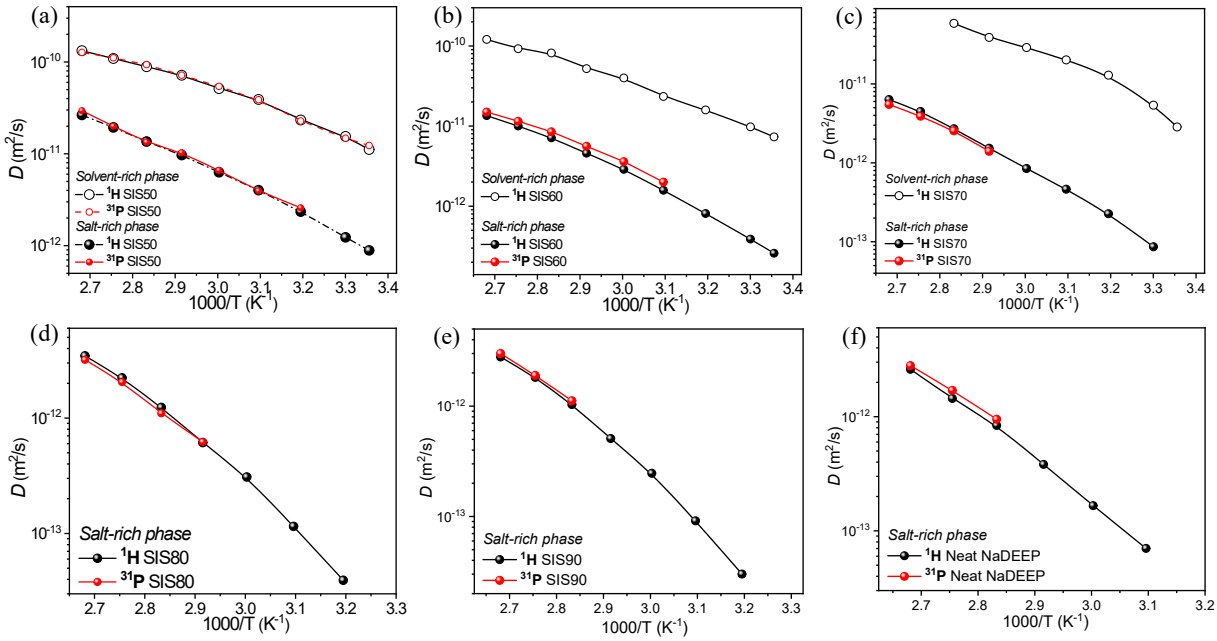

Figure S9. Diffusion coefficients obtained by the decomposition of ^{1}H NMR diffusion decays and ^{31}P NMR lines decays for (a-e) the SIS*XX* electrolytes and (f) the NaDEEP salt.

Table S1. Thermal decomposition (T_{decomp}) and glass transition (T_g) temperatures.

Sample	T_{decomp} (°C)	T_g (°C)
NaDEEP	225	–41
TEOP	237	–85
SIS50	236	–83
SIS60	241	–82
SIS70	249	–80
SIS80	270	/
SIS90	200	/

Table S2. VFT equation parameters and apparent activation energies for ionic conductivities for SIS*XX* electrolytes and NaDEEP.

System	σ_0 (m^2/s)	B (K)	T_0 (K)	E_σ(kJ/mol)
SIS50	0.0018	1005	150	8.4
SIS60	0.0027	994	154	8.3
SIS70*	0.0063	1050	160	8.7
SIS80	0.0122	918	162	7.6
SIS90	0.0467	1096	156	9.1
NaDEEP	0.2175	1428	155	11.9

* Only elevated temperature conductivity data were used in the VFT equation fit.

Table S3. Electrochemical stability of the TEOP solvent, the SIS*XX* electrolytes and the NaDEEP salt. Anodic and cathodic limits set to current density = ±0.1 mA cm^{-2}.

Sample	Anodic limit at 20 °C (V *vs.* Na/Na^+)	Cathodic limit at 20 °C (V *vs.* Na/Na^+)
TEOP	7.51	1.50
SIS50	7.82	1.74
SIS60	6.96	0.28
SIS70	6.61	1.46
SIS80	6.50	/
SIS90	5.84	/
NaDEEP	5.45	/

Table S4. Electrochemical stability of the TEOP solvent, the SIS60 and SIS90 electrolytes, and the NaDEEP salt at 20 °C and a current density of 0.05 mA cm^{-2}**.**

Sample	**Pt WE**		**GC WE**	
	Anodic limit (V *vs.* Na/Na^+)*	Cathodic limit (V *vs.* Na/Na^+)*	Anodic limit (V *vs.* Na/Na^+)*	Cathodic limit (V *vs.* Na/Na^+)*
TEOP	6.93	2.85	8.16	-2.65
SIS60	6.37	1.59	10.64	-5.76
SIS90	5.49	/	6.13	
NaDEEP	5.36	/	5.37	

Table S5. VFT equation parameters and apparent activation energies of diffusivity (^{1}H) for the SIS*XX* electrolytes, the NaDEEP salt, and the TEOP solvent.

Systems	Sub-system	$D_0 \times 10^{-9}$ (m^2/s)	B (K)	T_0 (K)	E_D (kJ/mol)
SIS50	Solvent-rich	1.44	356	225	3.0 ± 0.05
	Salt-rich	6.7	1100	175	9.1 ± 0.1
SIS60	Solvent-rich	1.44	356	232	3.0 ± 0.05
	Salt-rich	3.23	965	196	8.0 ± 0.1
SIS70	Solvent-rich	1.44	356	240	3.0 ± 0.1
	Salt-rich	2.5	870	209	8.1 ± 0.1
SIS80	Solvent-rich	3.01	1014	223	8.4 ± 0.1
	Salt-rich	/	/	/	/
SIS90	Solvent-rich	1.71	921	229	8.4 ± 0.1
	Salt-rich	/	/	/	/
NaDEEP	-	7.49	1279	213	10.6 ± 0.1
TEOP	-	5.11	379	222	3.2 ± 0.05

*For SIS80 and SIS90, the "salt-rich" VFT parameters could not be determined from the ^{1}H NMR spectra.