Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

$LiSi_3As_6$ and Li_2SiAs_2 with flexible $SiAs_2$ polyanions: Synthesis, structure, bonding, and ionic conductivity

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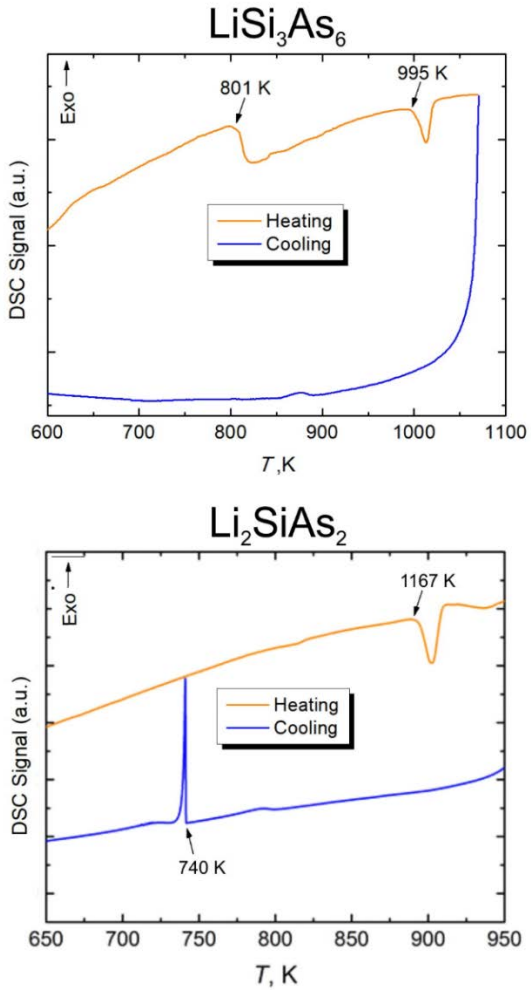

Figure S1. DSC measurements for $LiSi_3As_6$ (top) and Li_2SiAs_2 (bottom) with heating (orange) and cooling (blue) curves.

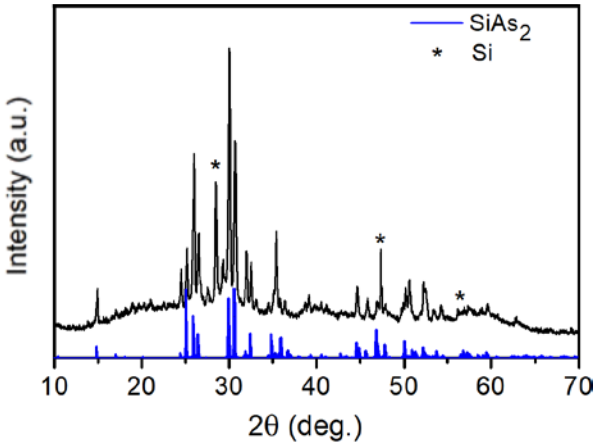

Figure S2. Powder diffraction pattern of a post-DSC sample of $LiSi_3As_6$. Theoretical pattern of $SiAs_2$ is shown as reference in blue, while Si peaks are labeled with star.

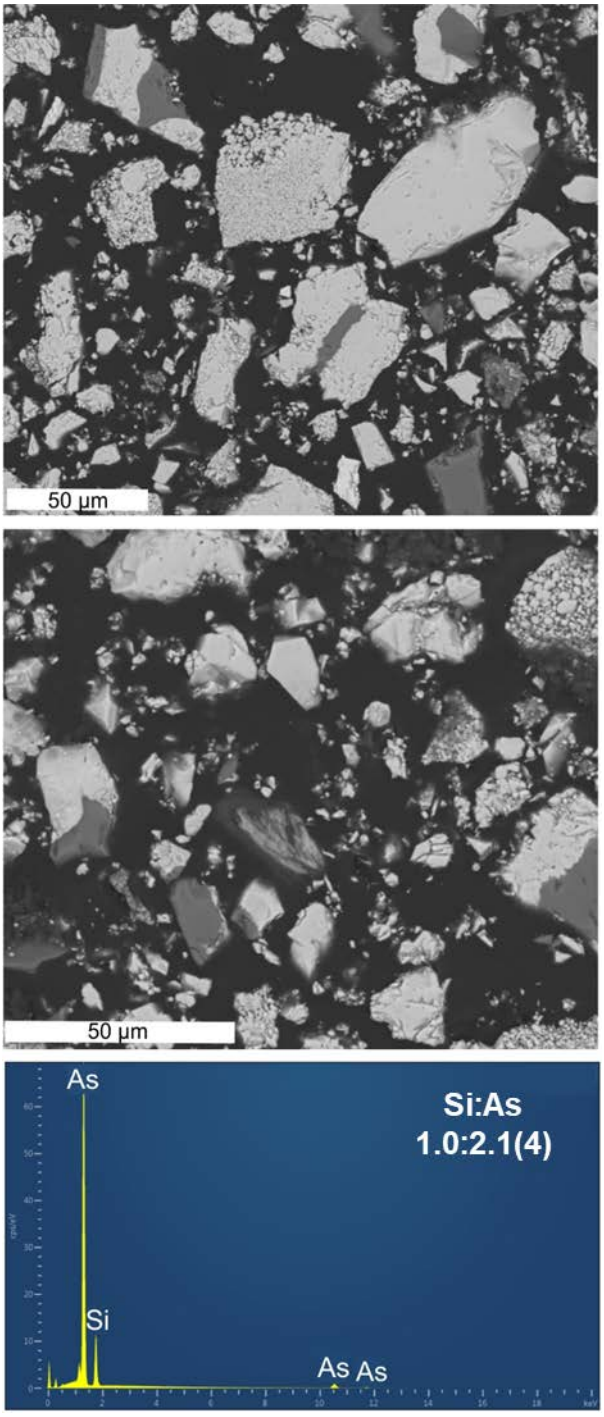

Figure S3. SEM images of a synthesized sample of $LiSi_3As_6$ mounted in epoxy (top/middle) and corresponding EDXS spectrum (bottom).

Table S1. Single crystal data collection and refinement parameters for $LiSi_3As_6$ and Li_2SiAs_2.

	$LiSi_3As_6$	Li_2SiAs_2
Space group	*Cmce* (no. 64)	$I4_1/acd$ (no. 142)
λ (Å)	Mo-*K*α: 0.71073	
T (K)	296(2)	90(2)
a (Å)	14.244(2)	12.563(4)
b (Å)	11.247(2)	
c (Å)	10.757(1)	19.390(6)
V (Å^{-3})	1723.3(4)	3060(2)
Z	8	32
ρ (g•cm^{-3})	4.17	3.33
μ (mm^{-1})	23.33	17.52
θ (°)	$2.99 < \theta < 27.49$	$3.11 < \theta < 33.25$
Data / param.	1029/50	1467/48
R_1	0.042	0.020
wR_2	0.088	0.034
Goodness-of-fit	1.03	1.10
Diff. peak/hole (e·Å^{-3})	1.33/–1.41	0.73/–0.68

Table S2. Atomic coordinates for $LiSi_3As_6$ and Li_2SiAs_2.

Atom	**Wyckoff Position**	***x/a***	***y/b***	***z/c***	U_{eq} (Å^2)
$LiSi_3As_6$					
As1	16*g*	0.13830(5)	0.16836(7)	0.08910(7)	0.0132(2)
As2	8*e*	¼	0.4312(1)	¼	0.0148(3)
As3	16*g*	0.08817(5)	0.31838(7)	0.93863(7)	0.0135(2)
As4	8*f*	0	0.9372(1)	0.2811(1)	0.0133(3)
Si1	8*f*	0	0.0518(3)	0.0944(3)	0.0126(6)
Si2	16*g*	0.1232(1)	0.3027(2)	0.2603(2)	0.0131(5)
Li1	8*d*	0.218(2)	½	0	0.041(6)
Li_2SiAs_2					
As1	32*g*	0.28410(2)	0.21850(2)	0.12773(2)	0.00529(5)
As2	16*d*	½	¼	0.97912(2)	0.00481(6)
As3	16*e*	¼	0.43770(2)	0	0.00445(6)
Si1	32*g*	0.38023(4)	0.33463(5)	0.05665(3)	0.0046(1)
Li1	16*f*	0.0939(3)	0.1561(3)	⅛	0.012(1)
Li2	16*f*	0.1557(4)	0.4057(4)	⅛	0.015(1)
Li3	32*g*	0.3778(3)	0.0961(3)	0.0340(2)	0.0137(8)

Table S3. Selected interatomic distances in $LiSi_3As_6$ and Li_2SiAs_2.

$LiSi_3As_6$			Li_2SiAs_2	
Atoms	Distance (Å)		Atoms	Distance (Å)
Si1-Si1	2.341(6)		Si1-As1	2.3424(8)
Si1-As1	2.367(2)		Si1-As1	2.3597(8)
Si1-As4	2.387(3)		Si1-As2	2.3778(7)
Si2-As1	2.392(2)		Si1-As3	2.3579(8)
Si2-As2	2.316(2)		Li1-As1	2.516(3)
Si2-As3	2.405(2)		Li2-As3	2.727(3)
Si2-As4	2.359(2)		Li3-As3	2.641(4)
As1-As3	2.445(1)			
As3-As3	2.512(2)			
Li1-As3	2.83(2)			

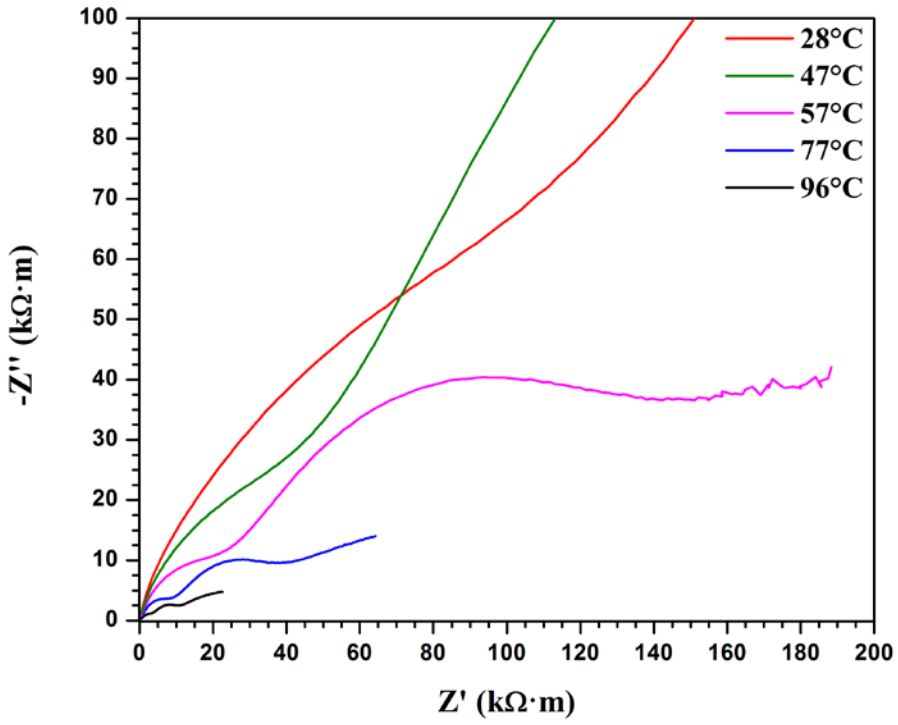

Figure S4. Nyquist plots of the impedance of Li_2SiAs_2 pellet measured at different temperatures.

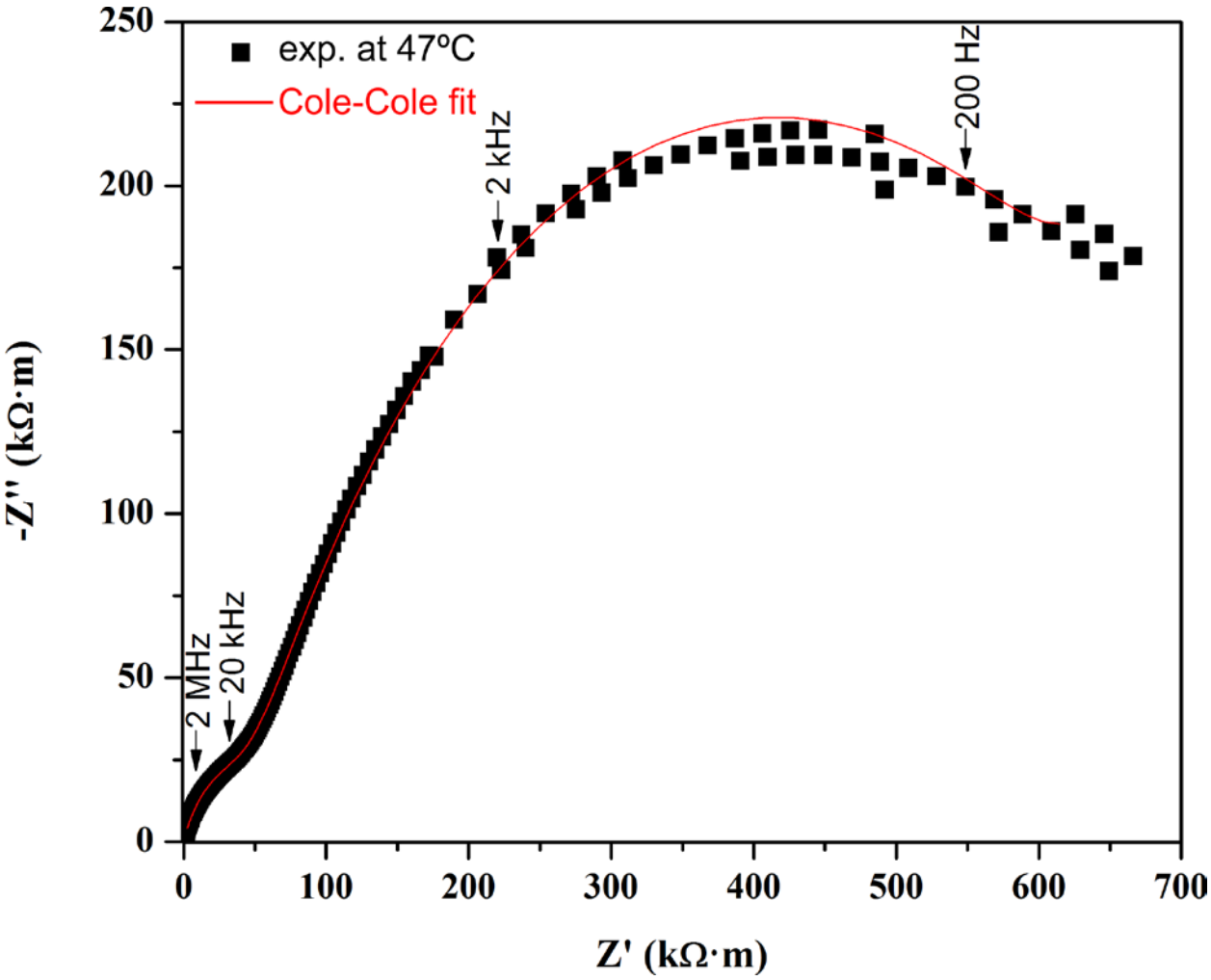

Figure S5. A representative fit for the Cole-Cole plot (red line) at 47°C. The small semicircle at 2 MHz is attributed to bulk conductive processes while the larger semicircle between 2 kHz and 200 Hz is from conductive processes across grain boundaries. The equivalent circuit used for fitting at all temperatures is composed of two parallel R-CPE circuits in series to represent the bulk and grain boundary contributions. The contribution for the electrode was modelled with a parallel R-CPE circuit, however there are not enough data points at low frequency to provide any meaningful or accurate estimates of the resistance or capacitance. At temperatures below 57°C the electrode contribution is not observable within the frequency range of the impedance measurement and was not included in the fitting procedure.