Supporting Information

Soft acid Bi^{3+} doping in Li_2ZrCl_6 to enhance ionic conductivity and electrochemical stability

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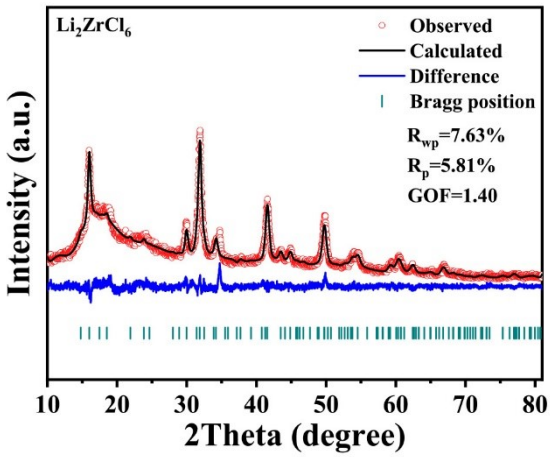

Fig. S1. Rietveld refinement results for LZC (experimental data represented by red dots, the black line indicates the calculated fit, the difference curve is shown in blue, and Bragg reflection positions are marked by vertical lines).

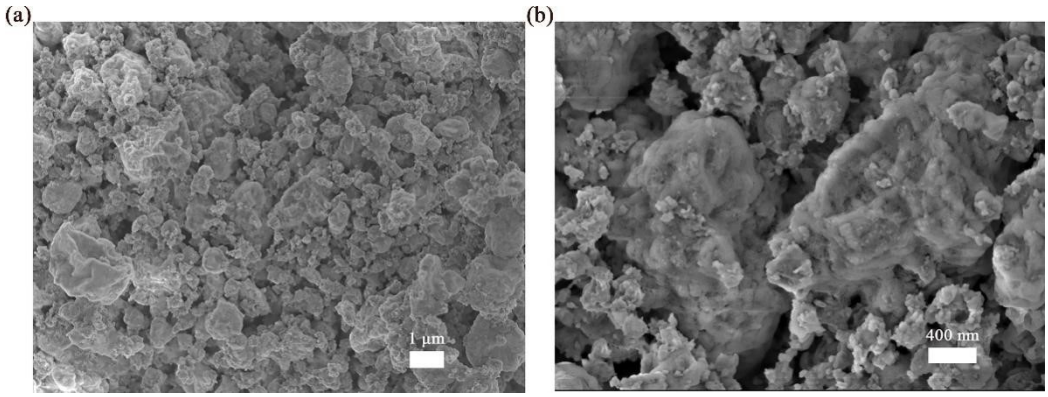

Fig. S2. (a-b) Scanning electron microscopy (SEM) images of LZC.

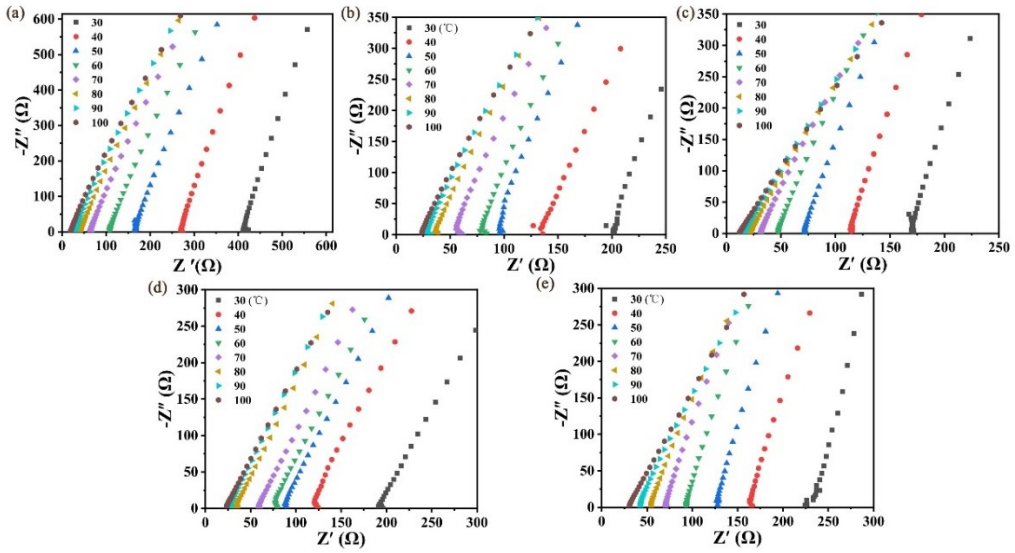

Fig. S3. The Nyquist plots (a-e) represent the high-frequency region of the $Li_{2+x}Zr_{1-x}Bi_xCl_6$ electrolyte at various temperatures for values of x equal to 0, 0.1, 0.15, 0.2, and 0.25.

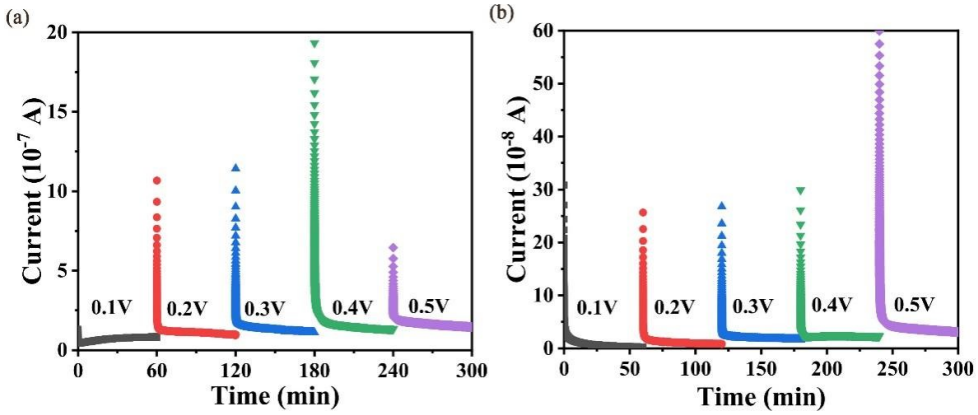

Fig. S4. Direct current (DC) polarization curves of (a) LZC and (b) LZBC at various voltages ranging from 0.1 to 0.5 V.

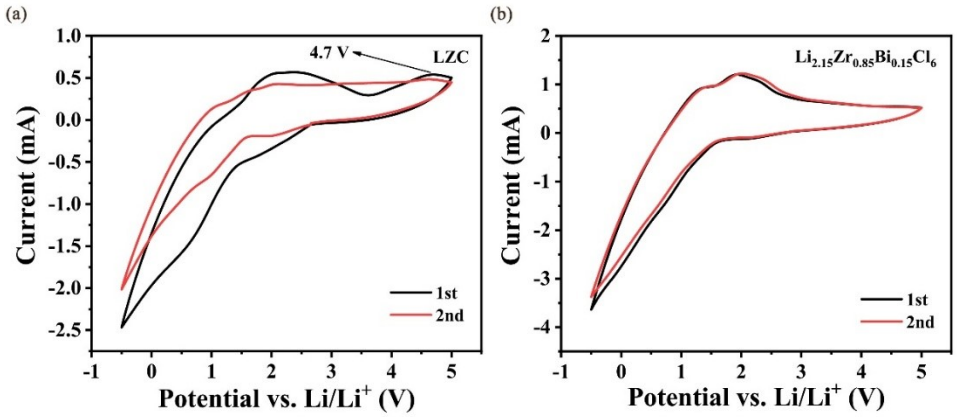

Fig. S5. The first two cyclic voltammetry (CV) curves of (a) LZC and (b) LZBC.

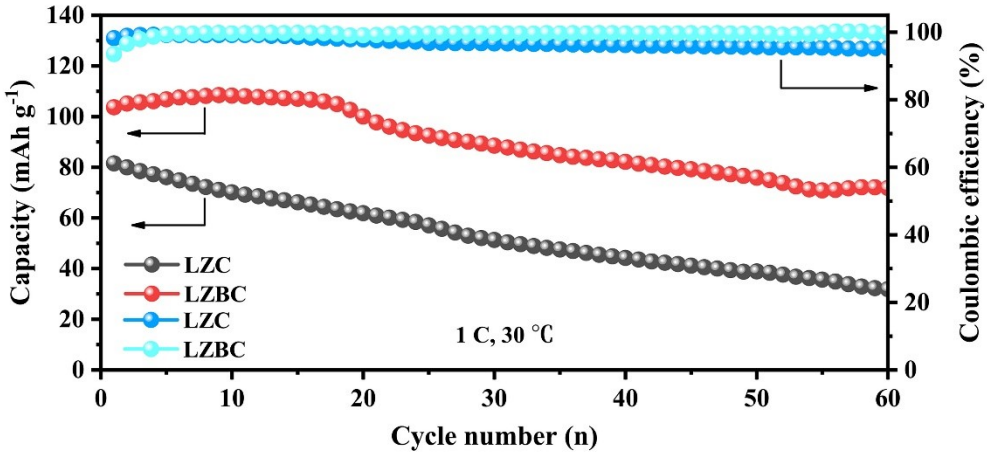

Fig. S6. The long-term cycling performance of ASSBs using LZC and LZBC as solid electrolytes

was evaluated at a voltage range of 2.5-4.5 V vs. Li^+/Li, at a temperature of 30℃ and a rate of 0.3C.

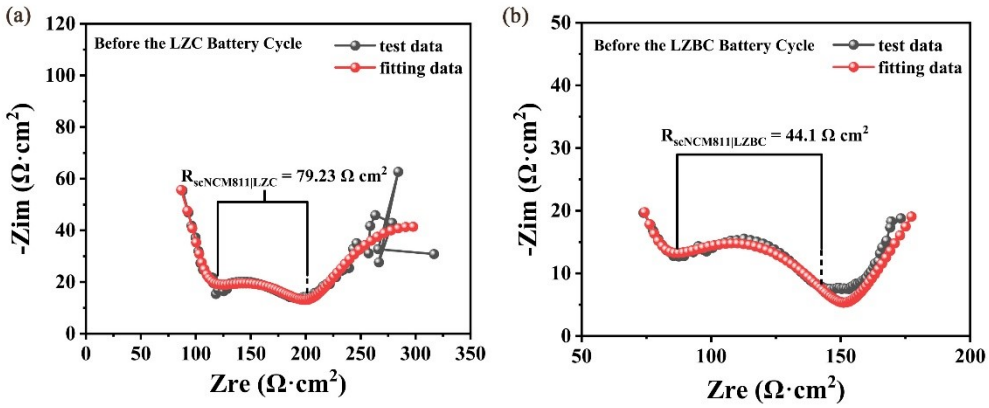

Fig. S7. (a) Impedance measurements and fitting results for LZC batteries and (b) LZBC batteries prior to cycling.

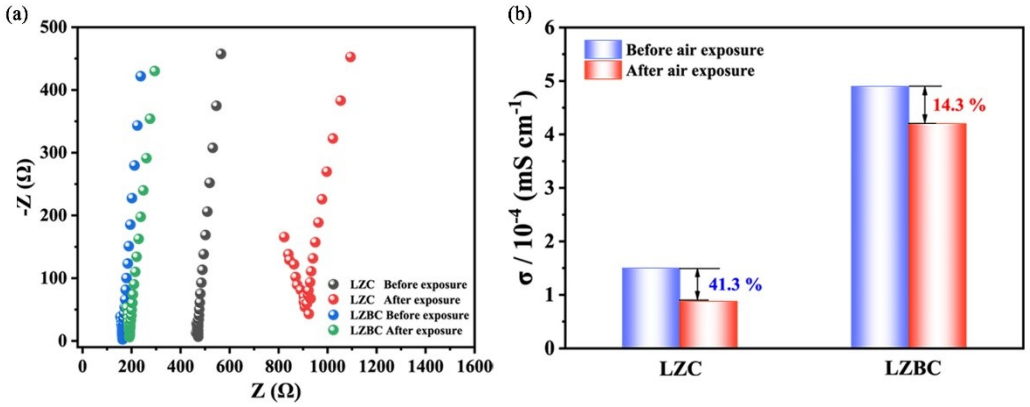

Fig. S8. (a) Impedance comparison between LZC and LZBC before and after exposure to air with a relative humidity of 50%. (b) Comparison of ionic conductivity before and after exposure.

Table S1. LZC and LZBC Lattice Parameters and Refinement Data.

Compound	**Li_2ZrCl_6**	**$Li_{2.15}Zr_{0.85}Bi_{0.15}Cl_6$**
Space Group	$P\bar{3}m1$	$P\bar{3}m1$
α=β=90°	γ=120°	γ=120°
a=b (Å)	10.9697(0)	11.0086(0)
c (Å)	5.9340(0)	5.9454(0)
c/a	0.54095	0.54003
Volume ($Å^3$)	618.39(7)	623.98(8)
R_{wp} (%)	7.63	6.79
R_p (%)	5.81	5.24
GOF	1.40	1.52

Table S2. XRD Refinement of Li_2ZrCl_6 Sample at Room Temperature.

Atomic position	**Wykoff site**	**x**	**y**	**z**	**Occ.**	**U**	**Sym**
Li1	6*g*	0.31061	0.00000	0.00000	0.208	0.065	2
Li2	6*h*	0.32121	0.00000	0.50000	0.792	0.065	2
Zr1	1*a*	0.00000	0.00000	0.00000	0.649	0.010	-3*m*
Zr2	2*d*	0.33333	0.66667	0.52682	0.525	0.010	3*m*
Zr3	1*b*	0.00000	0.00000	0.50000	0.756	0.010	-3*m*
Zr4	2*d*	0.33333	0.66667	0.94205	0.273	0.010	3*m*
Cl1	6*i*	0.11154	-0.11154	0.74153	1.000	0.007	*m*
Cl2	6*i*	0.22671	-0.22671	0.27190	1.000	0.007	*m*

Cl3	6*i*	0.44519	-0.44519	0.78561	1.000	0.007	*m*

Table S3. XRD Refinement of $Li_{2.15}Zr_{0.85}Bi_{0.15}Cl_6$ Sample at Room Temperature.

Atomic position	**Wykoff site**	**x**	**y**	**z**	**Occ.**	**U**	**Sym**
Li1	6*g*	0.31343	0.00000	0.00000	0.543	0.005	2
Li2	6*h*	0.31407	0.00000	0.50000	0.532	0.005	2
Zr1	1*a*	0.00000	0.00000	0.00000	0.634	0.077	-3*m*
Zr2	2*d*	0.33333	0.66667	0.50565	0.335	0.077	3*m*
Zr3	1*b*	0.00000	0.00000	0.50000	0.700	0.077	-3*m*
Zr4	2*d*	0.33333	0.66667	0.96396	0.273	0.077	3*m*
Bi1	1*a*	0.00000	0.00000	0.00000	0.112	0.077	-3*m*
Bi2	2*d*	0.33333	0.66667	0.50565	0.059	0.077	3*m*
Bi3	1*b*	0.00000	0.00000	0.50000	0.124	0.077	-3*m*
Bi4	2*d*	0.33333	0.66667	0.96396	0.048	0.077	3*m*
Cl1	6*i*	0.11618	-0.11618	0.74919	1.000	0.002	*m*
Cl2	6*i*	0.22633	-0.22633	0.27400	1.000	0.002	*m*
Cl3	6*i*	0.44597	-0.44597	0.78080	1.000	0.002	*m*

Table S4. The impedance spectrum fitting data were obtained in a state where the positive electrode was not charged. The fitting circuits and results are presented in Fig. S7a and 7b.

Sample	R1	Q1-Yo	Q1-n	R2	Q1-Yo	Q1-n	R3	Q1-Yo	Q1-n
LZC	121.2	8.597E-10	0.9965	79.2	1.508E-5	0.4224	107.8	0.00717	0.5350
LZBC	96.8	2.511E-10	0.9381	44.1	1.112E-5	0.3711	156.2	0.04056	0.3891

Table S5. The fitting date of impedance spectra at 100th cycles under the full charging state of positive electrodes. The fitting circuit and results are presented in Fig. 5a and 5b.

Sample	R1	Q1-Yo	Q1-n	R2	Q1-Yo	Q1-n	R3	Q1-Yo	Q1-n
LZC	203.74	8.625E-9	0.8256	129.7	8.541E-5	0.4857	395.5	0.01697	0.2599
LZBC	96.3	7.970E-9	0.7615	47.1	2.564E-5	0.3647	286.9	0.01046	0.2192