Supporting Information

Zirconia-supported solid-state electrolytes for high-safety lithium secondary batteries in a wide temperature range

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$$Zr(OC_4H_9)_4+4HCOOH = Zr(OOCH)_4+4C_4H_9OH$$

$$Zr(OOCH)_4+4C_4H_9OH = Zr(OH)_4+4C_4H_9COOH$$

$$HCOOH+C_4H_9OH = H_2O+C_4H_9COOH$$

$$Zr(OOCH)_4+4H_2O = Zr(OH)_4+4HCOOH$$

$$Zr(OOCH)_4+Zr(OH)_4 = 2ZrO_2+4HCOOH$$

$$Zr(OH)_4+Zr(OH)_4 = 2ZrO_2+4H_2O$$

Fig. S1 Chemical equations of resultant ZrO_2

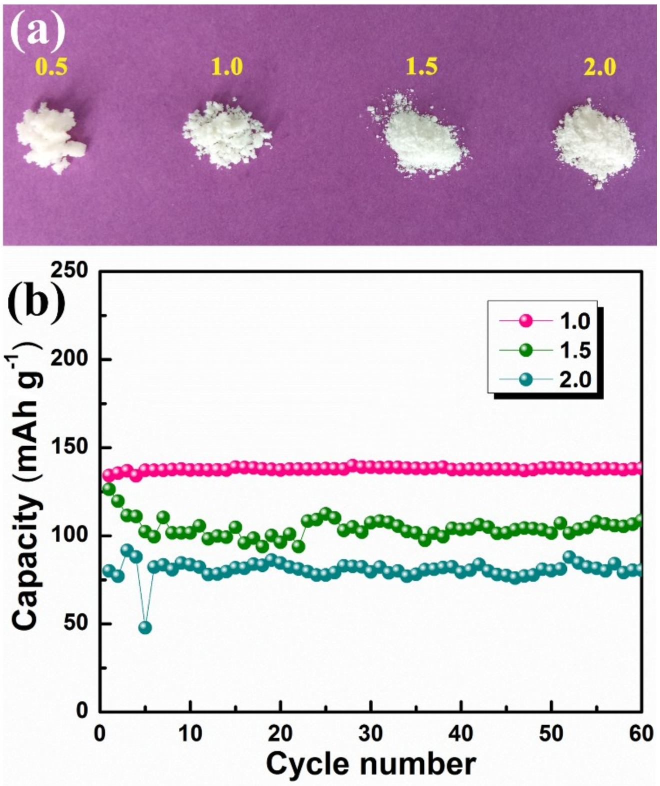

Fig. S2 (a) Digital photograph and (b) cycling performance of ZIEs with four different [EMI][TFSI]/ZrBO molar ratios (The cathodes, ZIE powders that were directly casted onto the cathodes and Li metal anodes were together pressed at 50 MPa to assemble 2025 coin cells. The ZIE with molar ratio of 0.5 can directly cause short circuit).

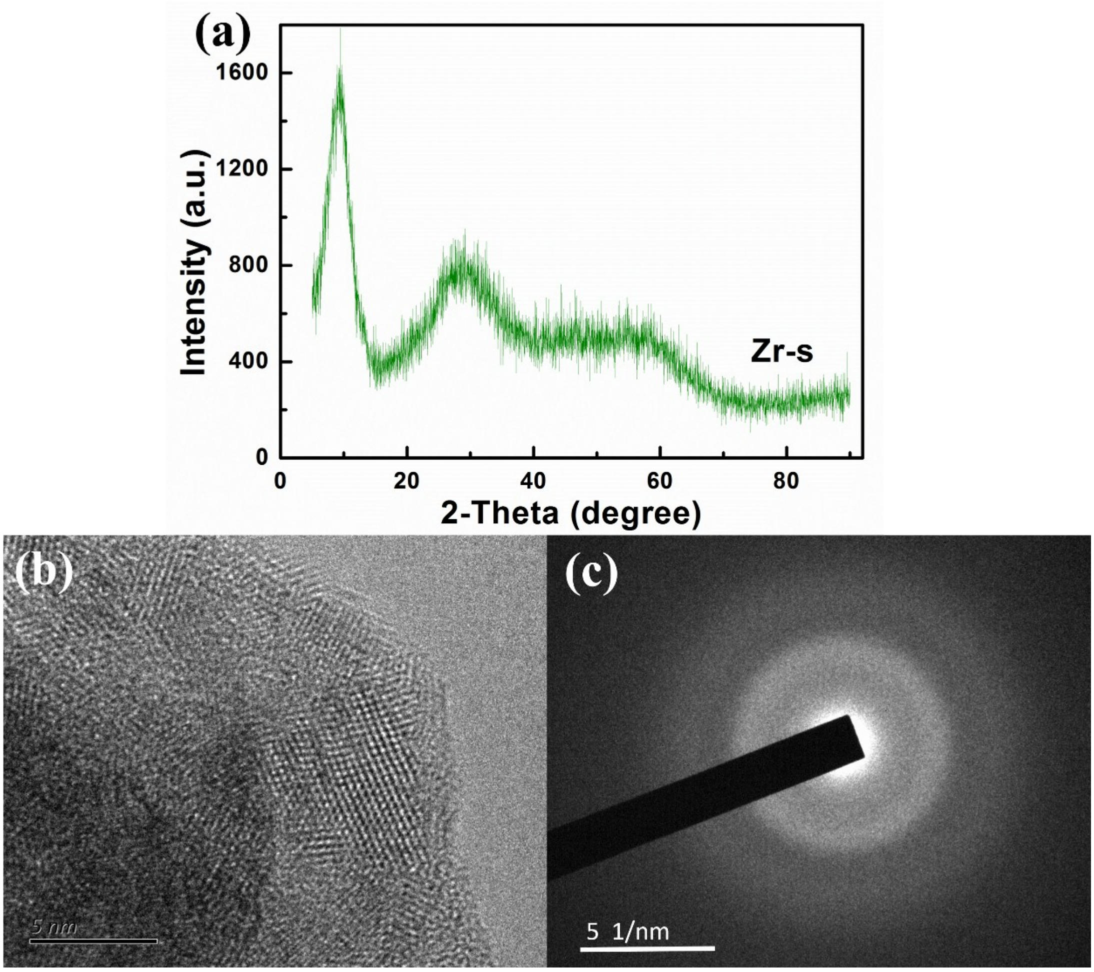

Fig. S3 (a) XRD pattern, (b) high resolution TEM and (c) electron diffraction images of Zr-s.

Table S1 Total energies of each structure involved in the computation process

Structure	Li^+	$TFSI^-$	LiTFSI	ZrO_2	ZrO_2-Li^+	ZrO_2-$TFSI^-$	ZrO_2-LiTFSI
Total Energy (eV)	5.47478	-64.17004	-64.12161	-344.69525	-346.44292	-407.04604	-409.74912

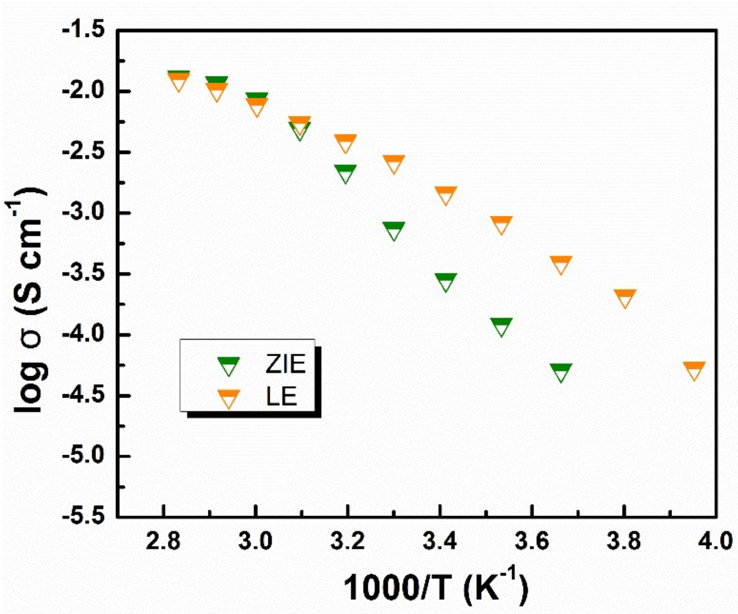

Fig. S4 Ionic Conductivity of ZIE and LE at various temperatures

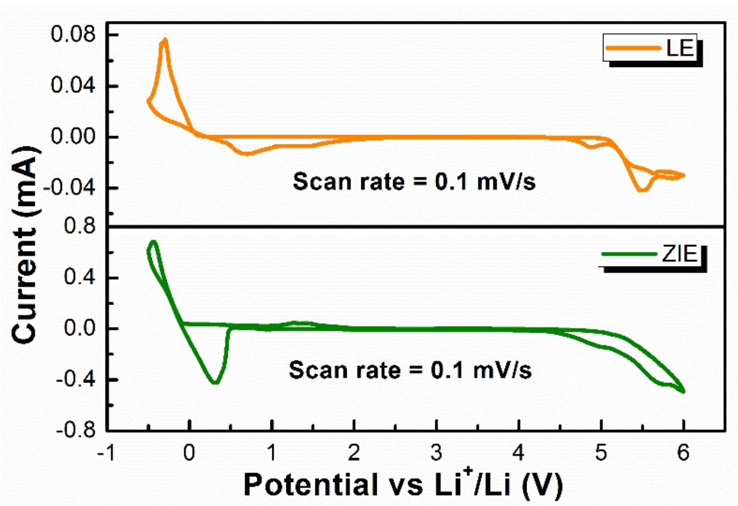

Fig. S5 Electrochemical stability window of ZIE and LE

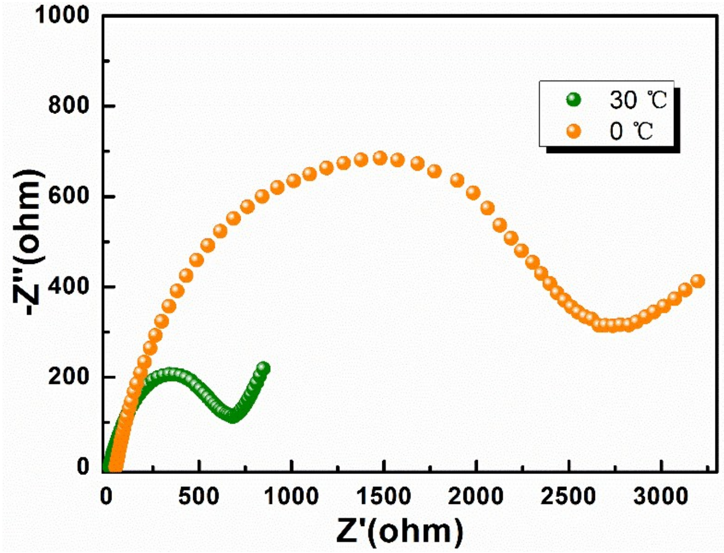

Fig. S6 EIS of the Li/ZIE/$LiFePO_4$ battery at 0 and 30 ℃

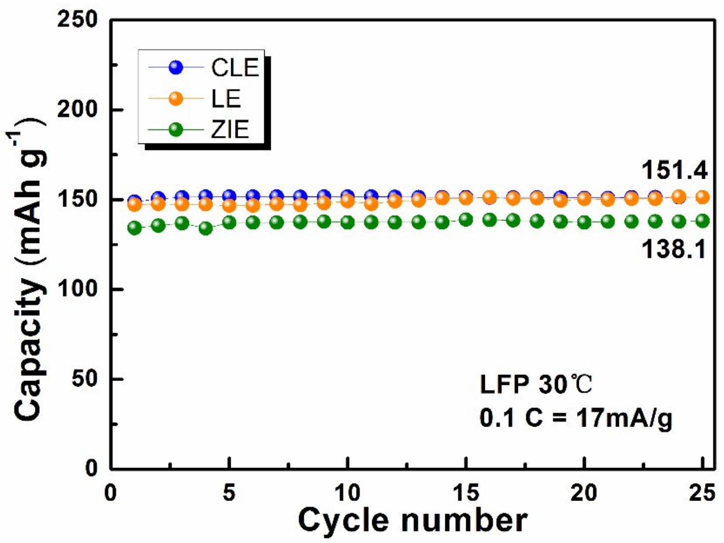

Fig. S7 Comparison of cycling performance of the Li/ $LiFePO_4$ batteries with ZIE, LE and conventional liquid electrolytes (CLE, 1 M $LiPF_6$ dissolved in ethyl carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume))at a 0.1 C rate at 30 ℃

Table S2 Performance comparison of different kinds of electrolytes used in LSBs

Electrolyte	Electrodes	Ionic Conductivity ($S\ cm^{-1}$, RT)	Cycles	Discharge Capacity ($mAh\ g^{-1}$)	Temperature range	Date	Ref.
ZIE	$LiFePO_4/Li$	7.43×10^{-4}	200	135.9 (30 ℃, 0.1 C)	–10~90 ℃	2017	
Conventional liquid electrolytes							
$LiPF_6$ (EC:DMC = 1:1)	$LiFePO_4/Li$	9.63×10^{-3}	20	151 (30 ℃, 0.1 C)	30 ℃	2017	
$LiClO_4$ (EC:DEC = 1:1)	$LiFePO_4$@C /Li		100	165 (25 ℃, 0.1 C)	25 ℃	2010	1
$LiPF_6$ (EC:PC:DEC =1:1:1)	$LiFePO_4$/artificial graphite	1.237×10^{-2}	100	341.4 (25 ℃, 1 C)	25~65 ℃	2010	2
	$LiFePO_4/Li$		3	147.8 (25 ℃, 0.1 C)			
$LiClO_4$ (PC:BS = 95:5)	$LiFePO_4/C$	4.55×10^{-3}	20	137 (25 ℃, 0.1 C)	25 ℃	2007	3
$LiBF_4$-LiBOB (PC:EC:EMC:MB=1:1:1:2)	$LiFePO_4/Li$	1.48×10^{-2}	100	79% of capacity retention (65 ℃, 1 C)	-40, 65 ℃	2014	4
LiFSI (EC:DMC =1:1)	$LiFePO_4/Li$	1.2×10^{-2}	100	137 (25 ℃, 1/12 C)	25 ℃	2009	5
Sulfide-based solid electrolytes							
PEO-LiTFSI-1%LGPS	$LiFePO_4/Li$	1.18×10^{-5}	50	137.4 (60 ℃, 0.5 C)	60 ℃	2016	6
PEO-LiTFSI-1%LGPS-10%SN	$LiFePO_4/Li$	9.10×10^{-5}	60	152.1 (40 ℃, 0.1 C)	25~60 ℃	2016	7
LGPS-LiG3	$LiFePO_4/Li$	About 6.0×10^{-3}	30	130 (30 ℃, 0.1 C)	30 ℃	2015	8
$75Li_2S$-$24P_2S_5$-$1P_2O_5$	$LiCoO_2/Li$	8.0×10^{-4}	30	109 (25 ℃, 0.1 C)	25 ℃	2016	9
$Li_{10}SiP_2S_{12}$	$Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2/Li$	2.3×10^{-3}	75	119 (30 ℃, 0.1 C)	30 ℃	2014	10
$78Li_2S$-$22P_2S_5$	FeS_2/Li	1.78×10^{-3}	50	560 (30 ℃, 0.05 C)	30 ℃	2017	11

(EC: ethylene carbonate, DMC: dimethyl carbonate, DEC: diethyl carbonate, PC: propylene carbonate, EMC: ethylmethyl carbonate, MB: methyl butanoate, BS: butylene sulfite, LiBOB: lithium bis(oxalato)borate, SN:succinonitrile, LGPS: $Li_{10}GeP_2S_{12}$, LiG3: Li(G3)TFSI, G3: triethylene glycol dimethyl ether)

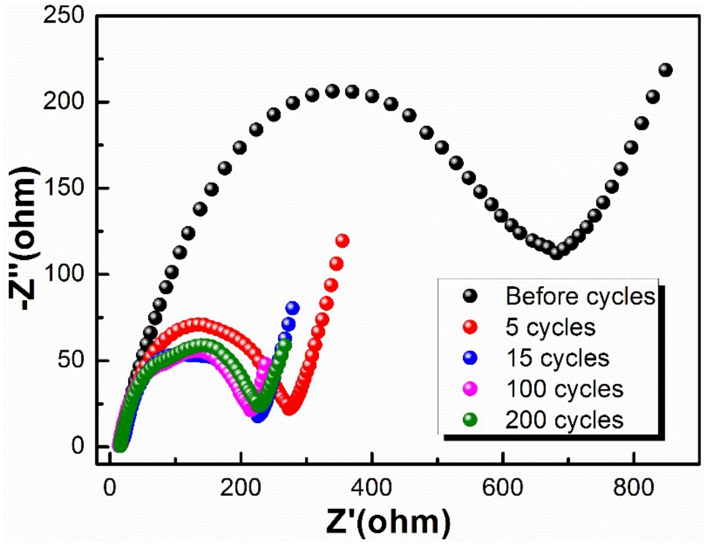

Fig. S8 EIS of the Li/ZIE/$LiFePO_4$ battery at different cycles

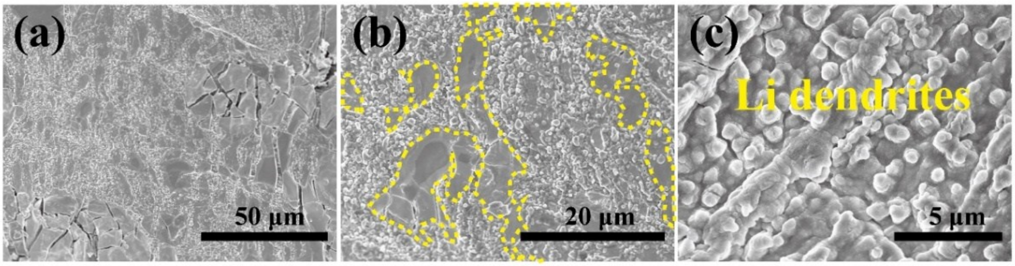

Fig. S9 SEM images of the surface of Li-metal anode in a Li/LE/$LiFePO_4$ battery after a few cycles

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