Supporting Information

High Performance Lithium Ion Electrolyte Based on a Three-dimensional Holey Graphene Frameworks Cross-linked with Polymer

Jialiang Xu[1,2], Ying Meng[2], Qihan Ding[2], Rui Wang[2], Tian Gan[1,2], Jiakui Zhang[2], Zhiping Lin[1] and Jiantie Xu[2]**

1. School of Physics and optoelectronic engineering, Guangdong University of Technology, Guangzhou 510006, China. E-mail: zhipinglphy@gdut.edu.cn

2. Guangdong Provincial Key Laboratory of Atmospheric Environment and Pollution Control, National Engineering Laboratory for VOCs Pollution Control Technology and Equipment, School of Environment and Energy, South China University of Technology, Guangzhou 510640, China E-mail: jiantiexu@scut.edu.cn

Keywords**:** Holey graphene; Polyethylene oxide; Solid state electrolytes; Li metal batteries.

1.1. Experimental section

Graphite oxide (GO) was prepared by a modified Hummers' method. Typically, 1 g graphite flakes and 6 g $KMnO_4$ were added into a mixture of concentrated 120 mL H_2SO_4 (98 wt%) and 13 mL H_3PO_4 (85 wt%). The resultant mixture was heated at 50 °C in oil bath and stirred for 24 h. When the mixture was cooled down to room temperature, it was poured into 400 mL ice water. The suspension was centrifuged and washed with DI water for several times to obtain GO with Mn species (Mn-GO) residual. Finally, the solution was dried in a freeze dryer for 72 h to obtain MnO-G foam. The holey graphene (hG) was synthesized by annealing MnO-G foam in Ar at 900 ^oC for 1 h with a heating rate of 20 ^oC min^{-1}, followed by a diluted 10 wt.% HCl wash to remove the MnO particles. For comparison, the graphene oxide (GO) foam was prepared by direct wash of Mn-GO by a diluted 10 wt.% HCl and then freezing-dried for 24 h. The mass yield of hG to GO is ~ 20 wt.%.

The PE-hG (PE-G and PE) films were prepared by mixing hG (GO), $LiNO_3$ (99.9%, Aldrich), polyvinyl pyrrolidone (PVP, $M_w = 5 \times 10^4$, Aldrich) and polyethylene oxide (PEO, $M_w = 1 \times 10^6$, Aldrich) with the methanol and then mechanically stirring for 24 h to form a homogeneous solution. The weight ratio of PEO, PVP, hG (x = 0, 1 and 2 wt. %)/G (x = 1 wt.%) and $LiNO_3$ for the fabrication of PEO (x =0), PE-hG/PE-G (x = 1), PE-2%hG (x = 2) films are 80 : 10 : x : 14, respectively. The solution was cast with a doctor blade on a polytetrafluoroethylene (PTFE) plate and dried in a vacuum oven at 60 °C for 24 h. Before its use in cells, the result electrolyte films were stored in a high purity Ar-filled glove box.

1.2. Materials Characterizations

The phases of the materials were analyzed by powder X-ray diffraction (XRD, Bruker D8 advance diffractometer) with Cu–Kα radiation (λ = 1.5406 Å). The morphologies and detailed structures of the samples were characterized by field emission scanning electron microscope (FESEM, Merlin, Zeiss) and transmission electron microscopy (TEM,

JEM2100). Raman spectra were recorded on a Raman spectrometer (Thermo Fischer DXR) using an excitation wavelength of 514 nm. Fourier transform infrared (FTIR) spectroscopy were recorded on Thermo iS50. Nitrogen adsorption–desorption isotherms were obtained from BELSORP-max (Micro for Tristar II Plus 2.02) and analyzed by using the Brunauer–Emmett–Teller (BET) method. X-ray photoelectron spectra (XPS) measurements were performed on an Escalab 250Xi X-ray photoelectron spectrometer using C 1 s (B.E. = 284.8 eV) as a reference.

1.3. Electrochemical measurements

The electrochemical characterization of the symmetric or asymmetric cells were fabricated in 2032-type coin cells. The symmetric (*e.g.*, Li||PE-hG||Li and SS||PE-hG||SS) and asymmetric cells (*e.g.*, $LiFePO_4$||PE-hG||Li and SS||PE-hG||Li) were by the use of Li metal as anode/electrode, the as-prepared SSEs (*e.g.*, PE-hG) and a Li/$LiFePO_4$ as cathode/electrode, respectively. The $LiFePO_4$ cathode was prepared by blending 80 wt% $LiFePO_4$, 10 wt% carbon black, and 10 wt% PEO binder in the presence of methanol. The obtained slurry was coated on aluminum substrate and dried in vacuum oven at 80 ^oC for 12 h. The mass of punched $LiFePO_4$ electrode was controlled with 1 mg cm^{-2}. The the symmetric and asymmetric cells were assembled in an Ar-filled glove box and then housed at 80 °C for 24 h to reduce the interfacial impedance between electrode and electrolyte.

The Li transference number (t^+) of the SSEs in Li||PE-hG||Li cell was measured by chronoamperometry and AC impedance spectra. 10 mV was the potential applied. Electrochemical impedance spectroscopy (EIS) spectra of all cells were measured from 0.1 to 10^6 Hz. The t^+ values were calculated according to the equation as follows:

$$t^+ = I_{SS}(\Delta V - I_0R_0)/I_0(\Delta V - I_{SS}R_{SS})$$

where I_0 (I_{SS}), ΔV, R_0 (R_{SS}) are the currents at initial(steady)-state, the polarization potential at 10 mV, and resistance at initial(steady)-state, respectively. The ionic conductivities of SSEs

were evaluated by the EIS measurements between 30 and 90 °C. The electrolyte resistance (R_b') equals the internal resistance obtained from the EIS spectra. Electronic conductivity was measured by the DC polarization method at a constant voltage of 0.1 V for 1000 s at 80 °C. According to the steady-state current value and the applied external voltage value, the electronic resistance of the electrolyte (R_b'') can be calculated. The SSEs films were sandwiched by two stainless steel (SS) disks. The equation for calculating the ionic and electronic conductivities are described as follows:

$$\delta = l/SR_b$$

where l, S *and* R_b are the thickness of the electrolyte, the bulk resistance of the electrolyte ($R_b'$and R_b''), and the area of the electrodes, respectively. Linear sweep voltammetry (LSV) of Li||SSEs||SS cells was tested from 3.0 to 6.5 V. All the asymmetric cells were tested between 2.4 and 3.8 V at 80 °C. The electrochemical tests of symmetric and asymmetric cells were carried out using a CHI 760C (CH Instruments, USA). The battery was measured by using on an automatic battery tester system (Land®, China).

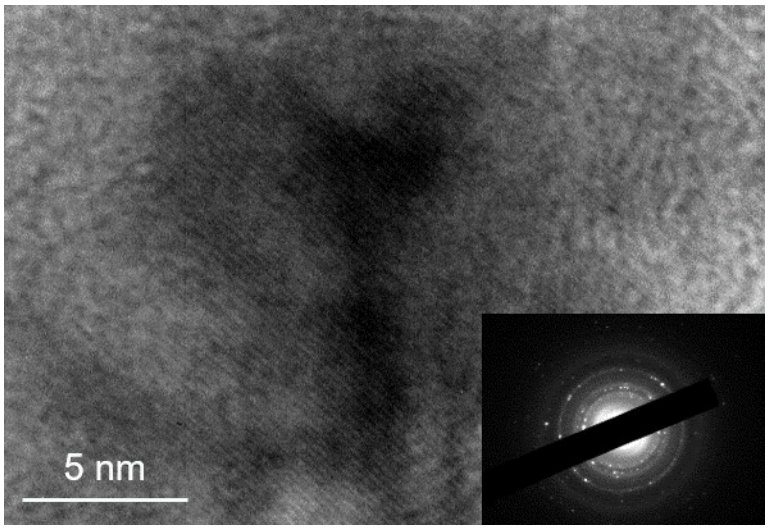

Figure S1. TEM image of MnO-G and its SAED.

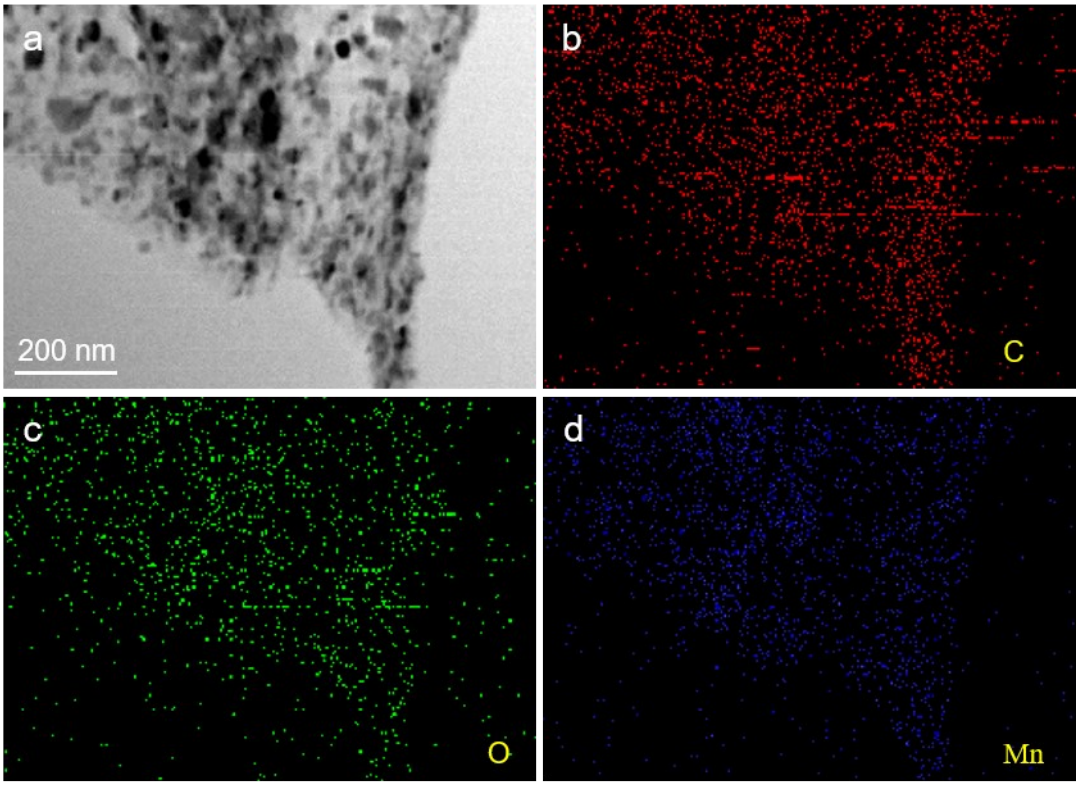

Figure S2. TEM element mappings of MnO-G: (b) C, (c) O and (d) Mn.

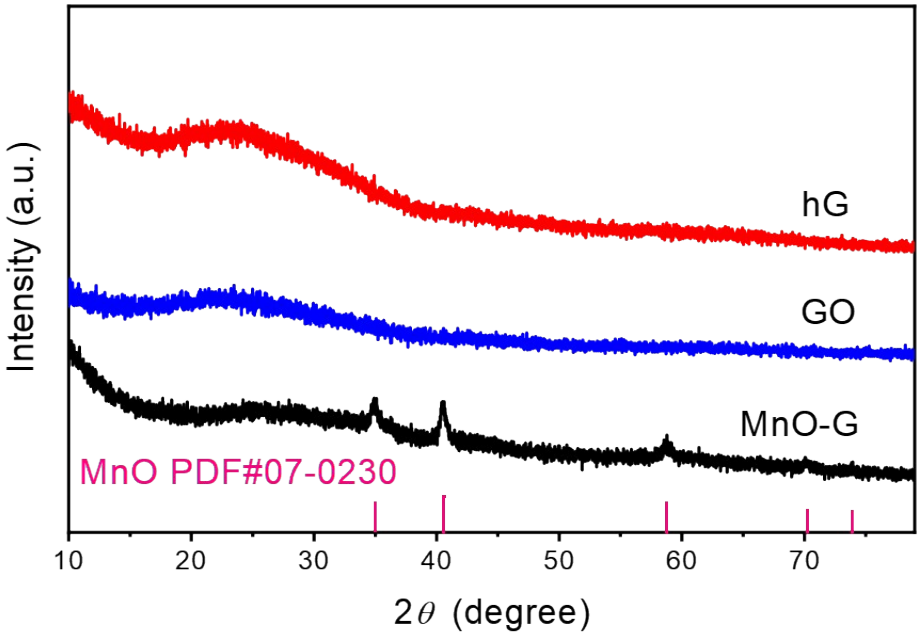

Figure S3. XRD patterns of hG, GO and MnO-G.

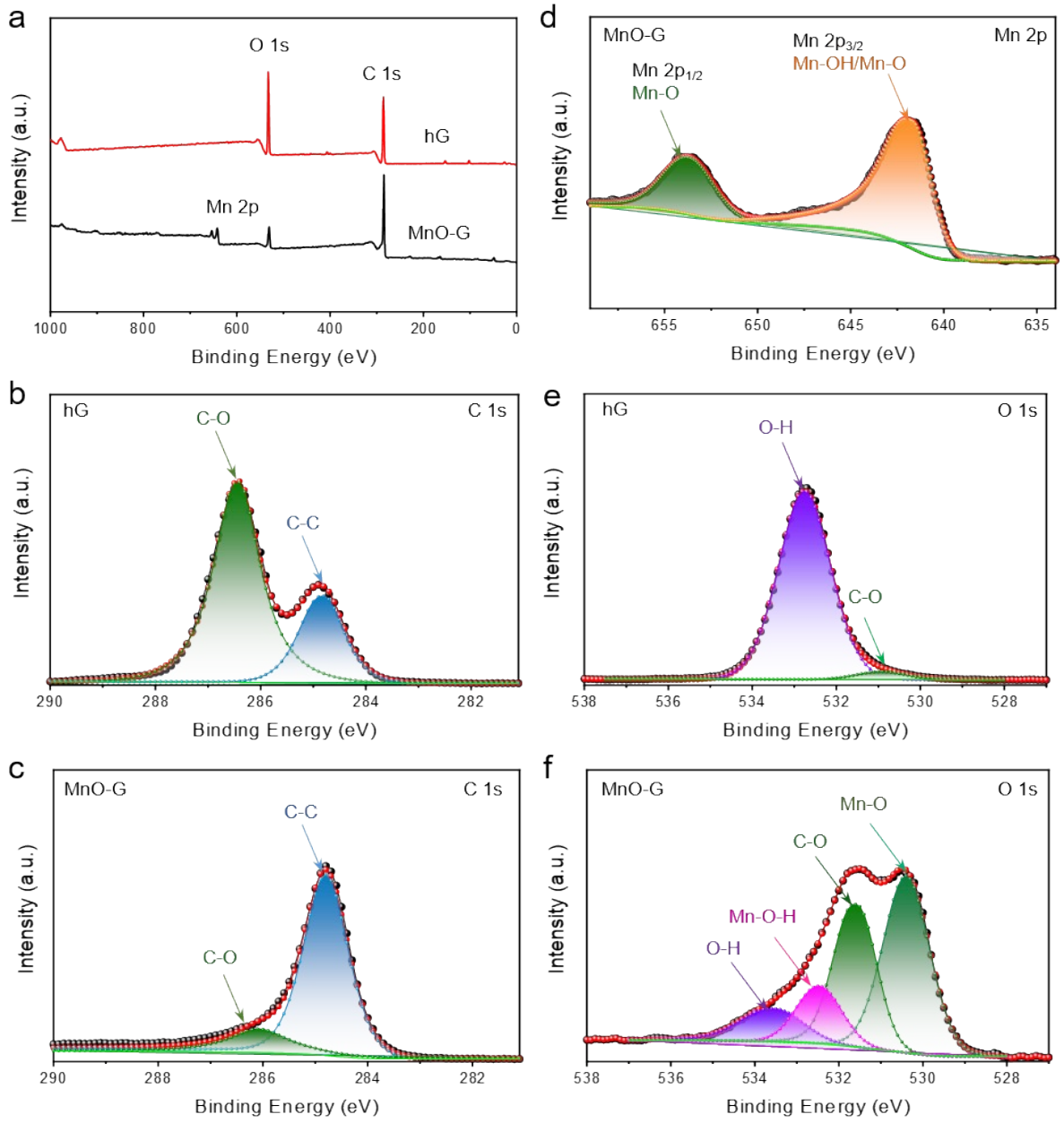

Figure S4. (a) Full-survey XPS spectra of hGO and MnO-G. High-resolution XPS spectra of hG: (b) C 1 s and (c) O 1 s, and MnO-G: (d) Mn 2p, (e) O 1s and (f) O 1s.

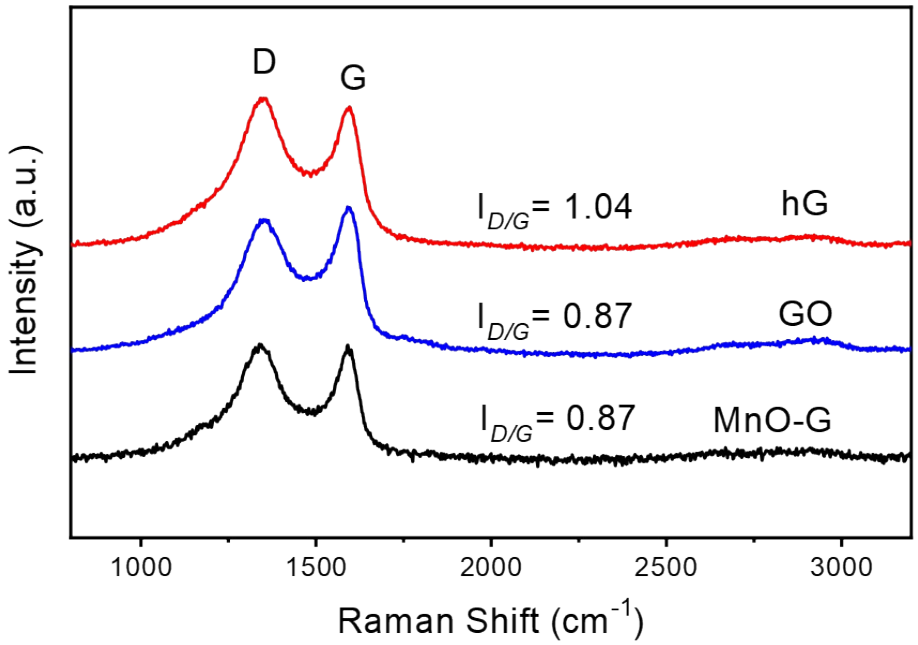

Figure S5. Raman spectra of hG, GO and MnO-G.

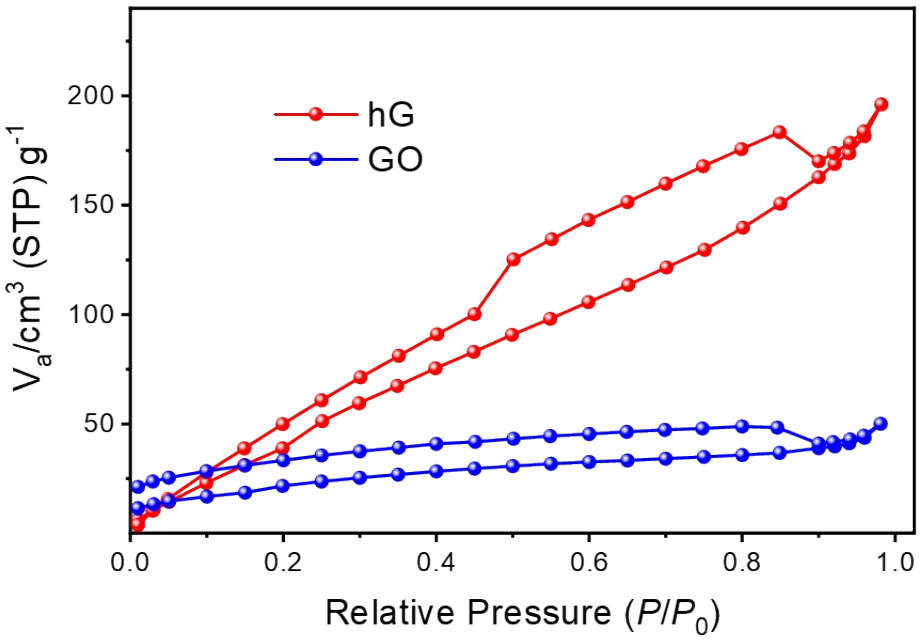

Figure S6. Nitrogen adsorption–desorption curves of hG and GO.

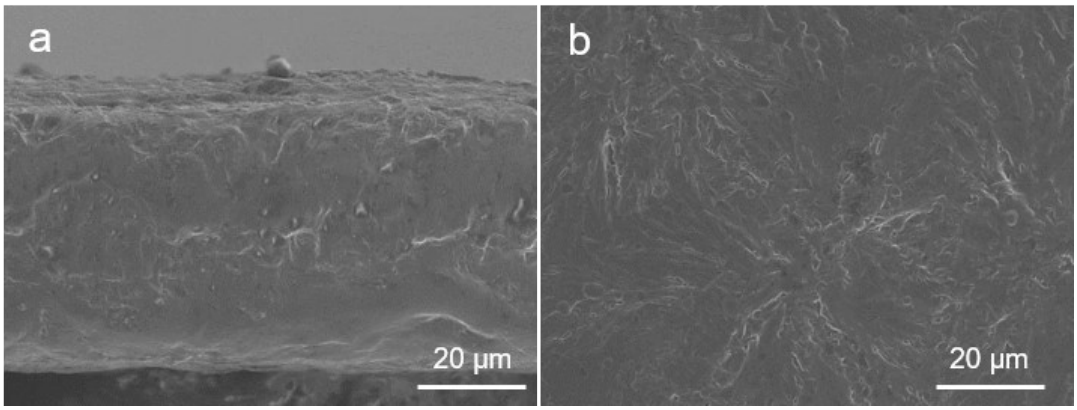

Figure S7. (a) Side-view and (b) top-view SEM images of PE film.

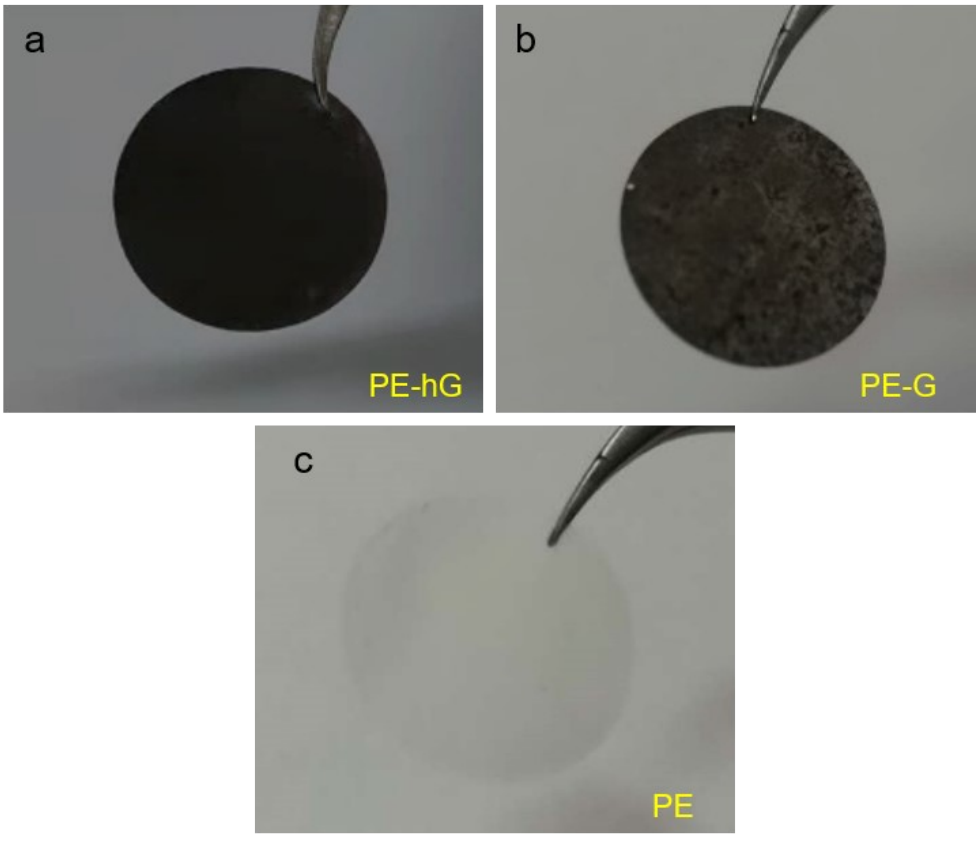

Figure S8. The digital photos of (a) PE-hG, (b) PE-G and (c) PE film.

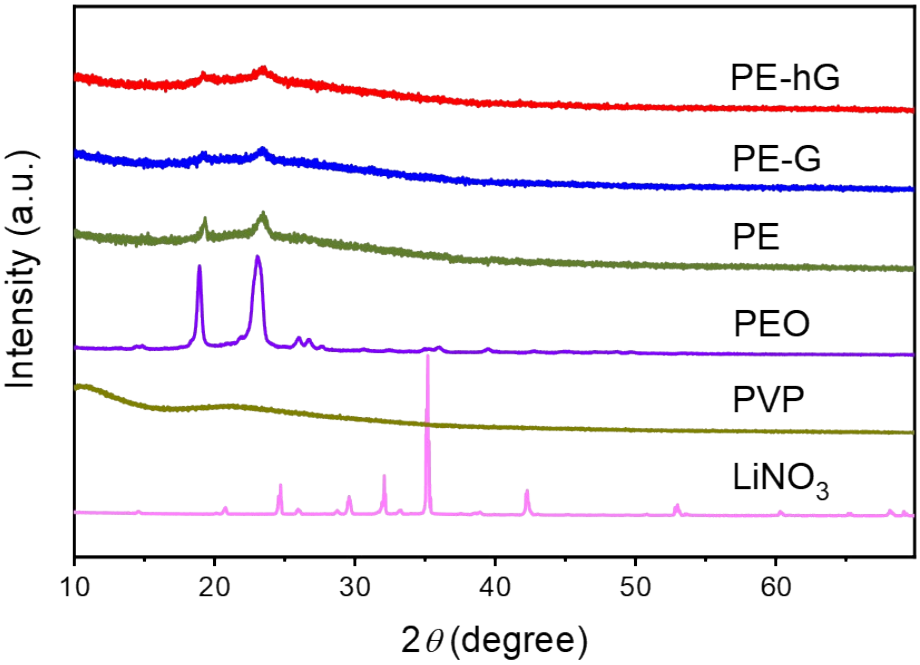

Figure S9. XRD patterns of PE-hG, PE-G, PE, PEO, PVP and $LiNO_3$.

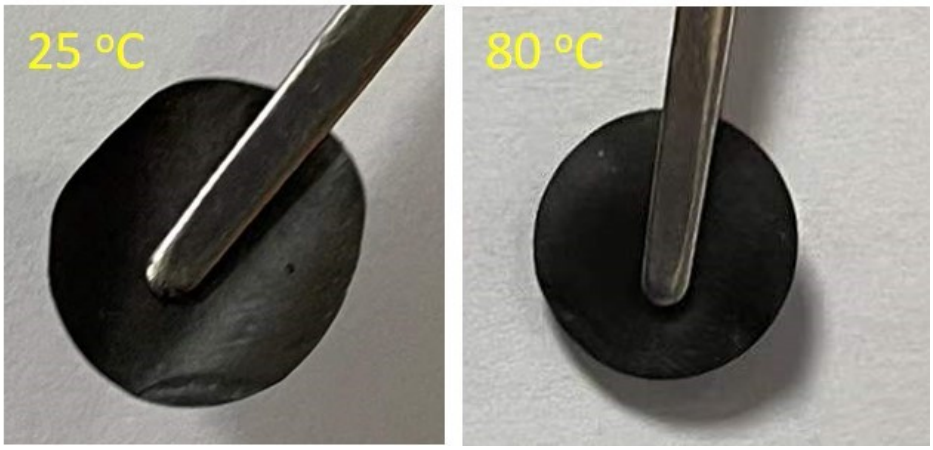

Figure S10. Digital photos of PE-hG electrolyte film at 25 °C and 80 °C.

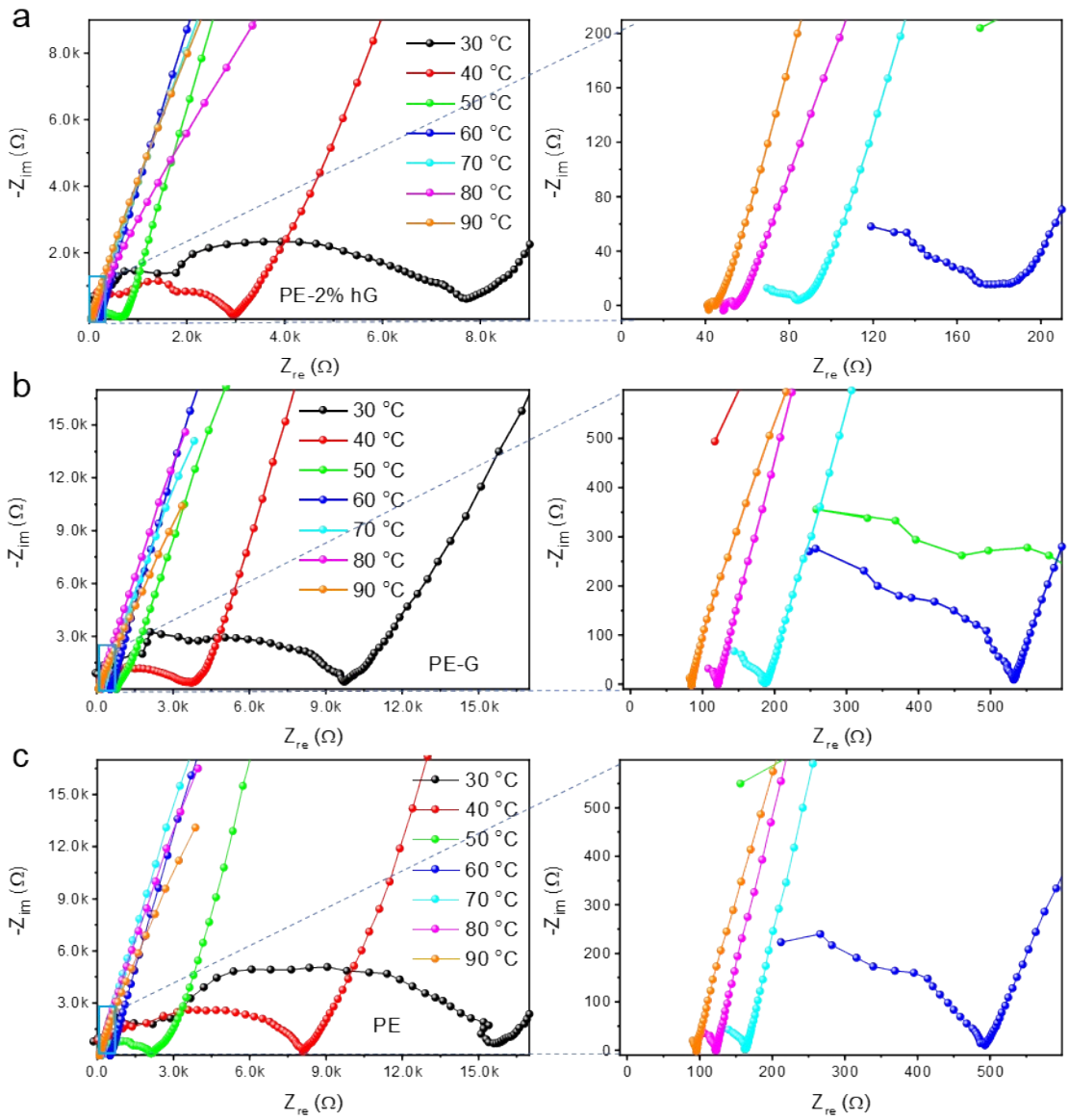

Figure S11. EIS spectra of symmetric SS||SSEs||SS cells using (a) PE-2% hG, (b) PE-G and (c) PE as electrolytes at various temperatures.

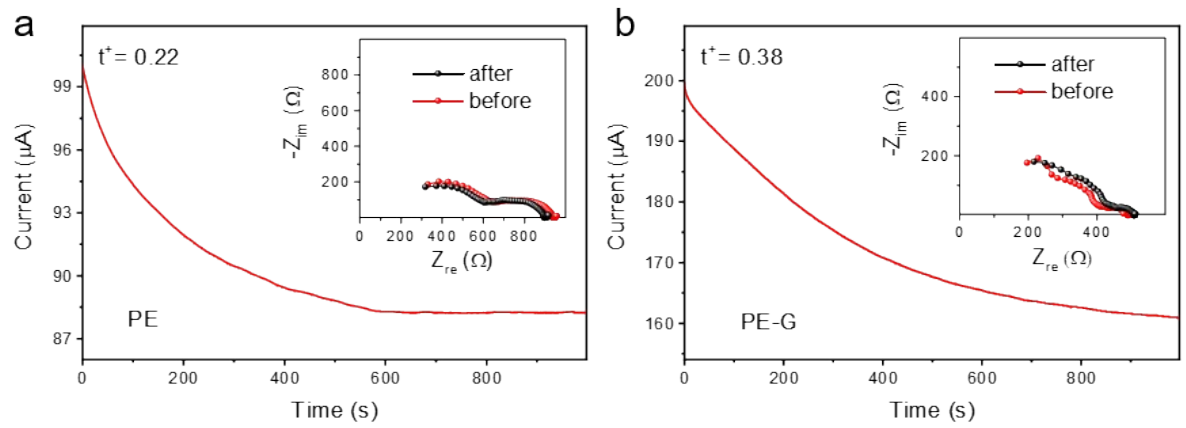

Figure S12. Chronoamperometry curves with a potential step of 10 mV of Li||SSEs||Li cells using (a) PE and (b) PE-G as electrolytes at 80 °C. Inset of Figure: EIS spectra of symmetric Li||SSEs||Li using PE and PE-G electrolytes before and after polarization.

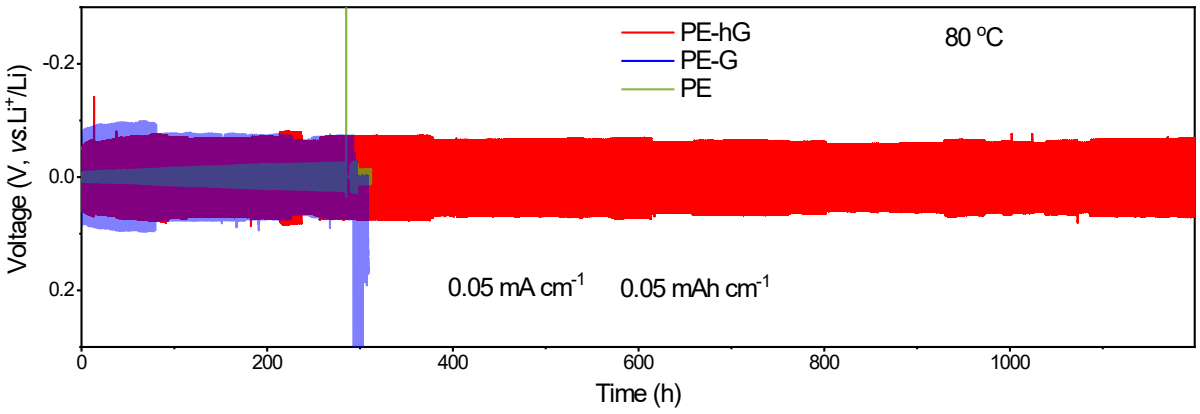

Figure S13. Voltage–time profiles of Li||PE-hG||Li, Li||PE-G||Li and Li||PE||Li cells at 0.05 mA cm^{-2} with a fixed capacity of 0.05 mAh cm^{-2}.

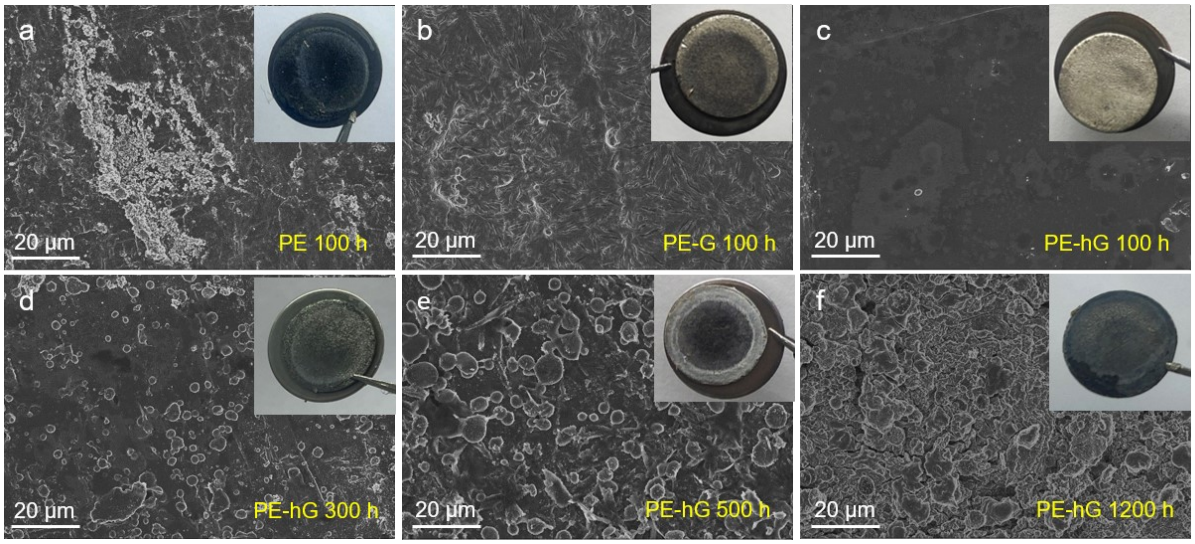

Figure S14. SEM images of Li surface with (a) PE, (b) PE-G and (c) PE-hG as electrolytes after 100h, and (d) PE-hG as electrolyte after 300, 500 and 1200 h, in symmetric Li||Li cells at 0.05 mA cm^{-2} after 100 h.

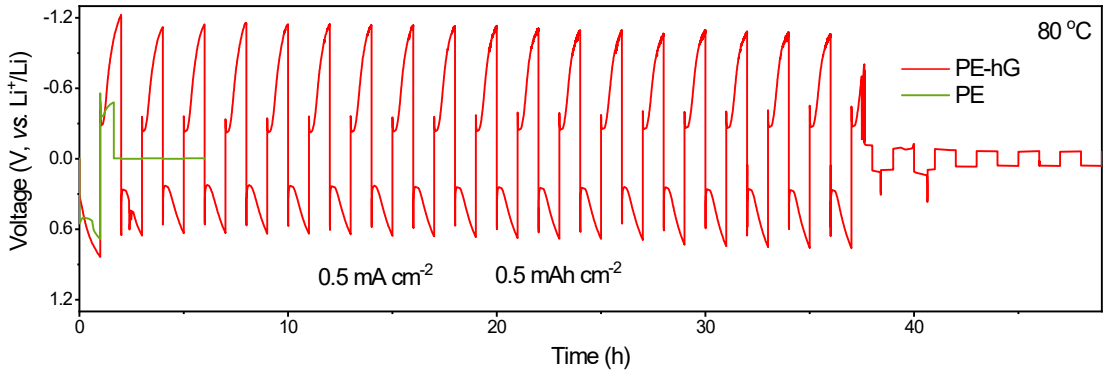

Figure S15. Voltage–time profiles of symmetric Li||PE-hG||Li and Li||PE||Li cells at 0.5 mA cm^{-2} with a fixed capacity of 0.5 mAh cm^{-2}.

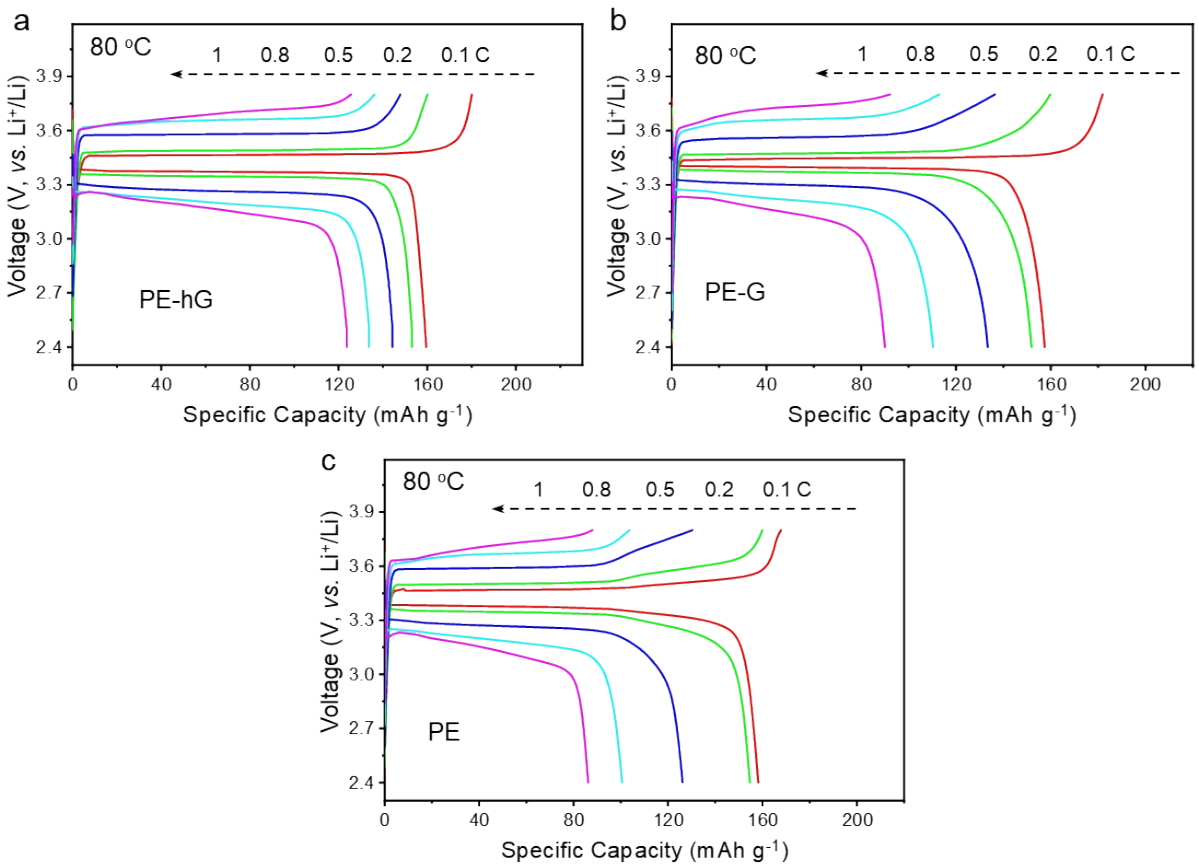

Figure S16. Charge–discharge curves of (a) $LiFePO_4$||PE||Li, (b) $LiFePO_4$||PE-G||Li and (c) $LiFePO_4$||PE-hG||Li cells measured at 0.1, 0.2, 0.5, 0.8 and 1 C.

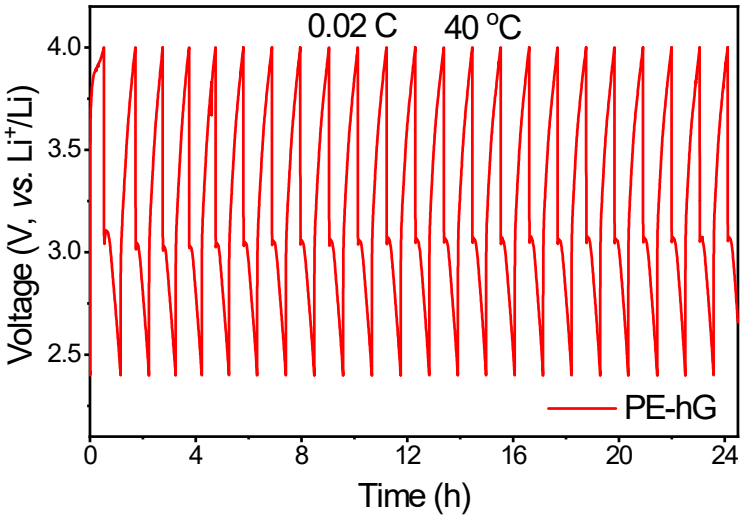

Figure S17. Voltage–time profiles of asymmetric $LiFePO_4$||PE-hG||Li cell at 0.02 C.

Table S1. Raman spectral data of PEO, PVP, PE, PE-G and PE-hG**.**

Band assignments	Raman Shift (cm^{-1})		
	PE-hG	**PE-G**	**PE**
G	1650	1650	-
CH_2 wagging (ω)	1470	1470	1470
D	1350	1350	-
CH_2 symmetric twisting (τ)	1280	1280	1280
C-N stretching	1230	1230	1230
Symmetric and asymmetric C-O-C stretching vibration (ν_s)	1050	1050	1050

Table S2. FTIR spectral data of PEO, PVP, PE, PE-G and PE-hG.

Band assignments	Wavenumber (cm^{-1})				
	PEO	**PVP**	**PE-hG**	**PE-G**	**PE**
Symmetric C-H stretching	2884	2902	2888	2886	2886
CO stretching	–	1660	1656	1650	1650
CH_2 stretching (ν)	962	–	962	962	962
CH_2 wagging (ω)	1342	–	1342	1342	1342
Asymmetric CH_2 twisting (τ)	1280	–	1280	1280	1280
CH_2 symmetric twisting (τ)	1241	–	1241	1241	1241
Symmetric and asymmetric C-O-C stretching vibration (ν_s)	1101	–	1101	1101	1112
CH_2 rocking in PVP and with some C-O stretching in PEO	845	849	845	845	845

Table S3. R_{ct} data of PE-hG, PE-2% hG, PE-G and PE at 30-90°C**.**

Temperature/°C	R_{ct}/Ω			
	PE	PE-G	PE-2% hG	PE-hG
90	95.3	84.5	44.5	32.5
80	122.2	121.2	52.7	35.5
70	262.5	187.3	83.8	54.1
60	593.3	432.7	183.4	74.6
50	2110.1	858.9	638.6	539.5
40	8090.8	3720.6	2960.3	2455.5
30	15600.9	9720.2	7710.2	5568.6