Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

$BaTiO_3$-g-GO as an efficient permselective material for lithium-sulfur batteries

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Synthesis of $BaTiO_3$-g-GO

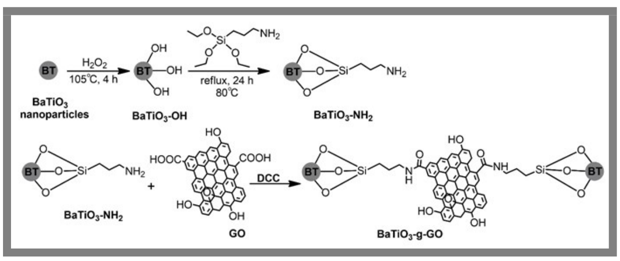


Figure SI 1a. Synthesis of $BaTiO_3$-g-GO.

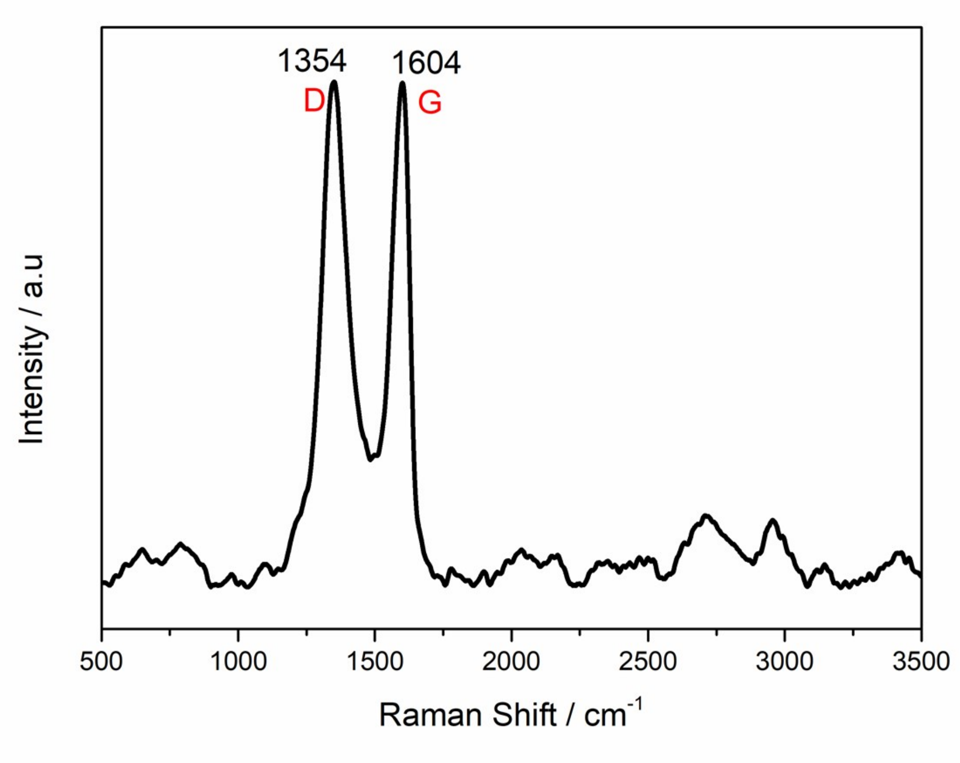


Figure SI 1b. Raman spectrum of synthesized Graphene Oxide.

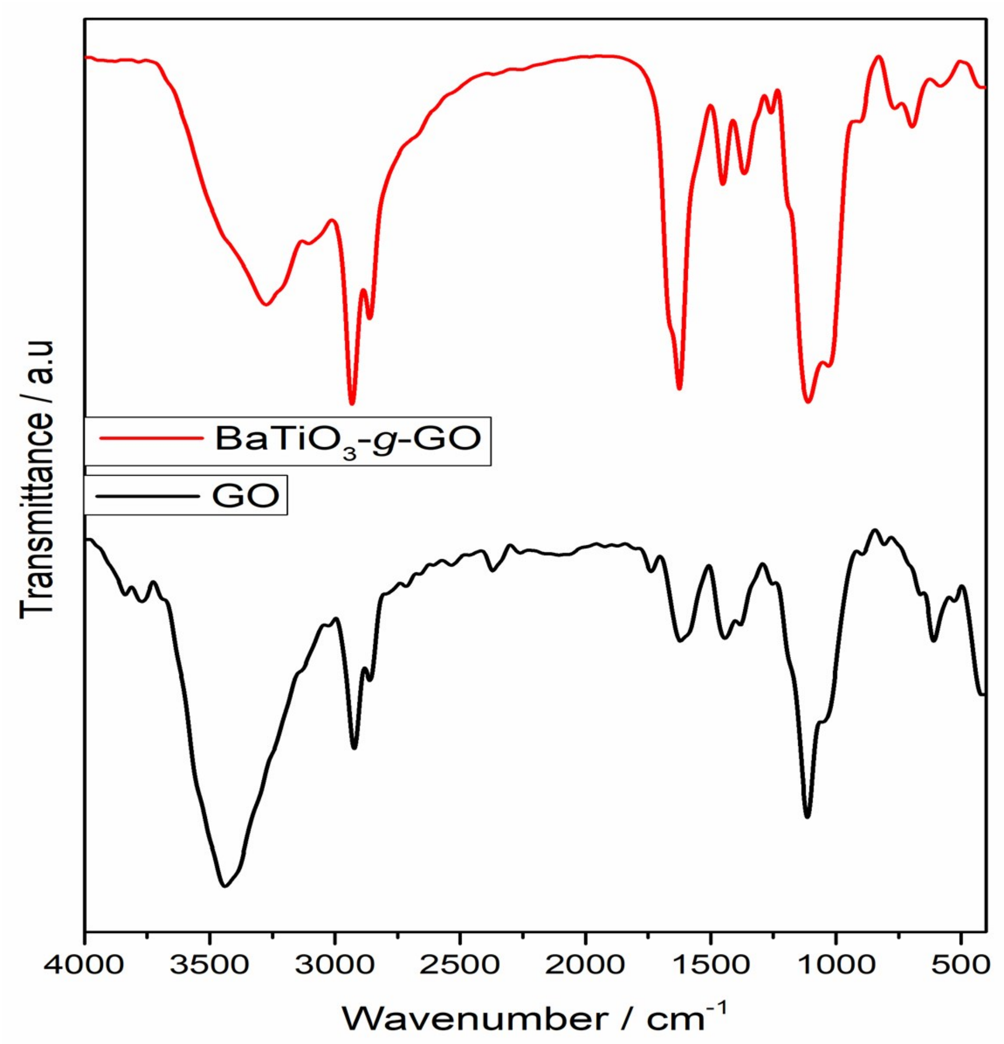


Figure SI 1c. The FT-IR spectra of GO and $BaTiO_3$-g-GO

EDX

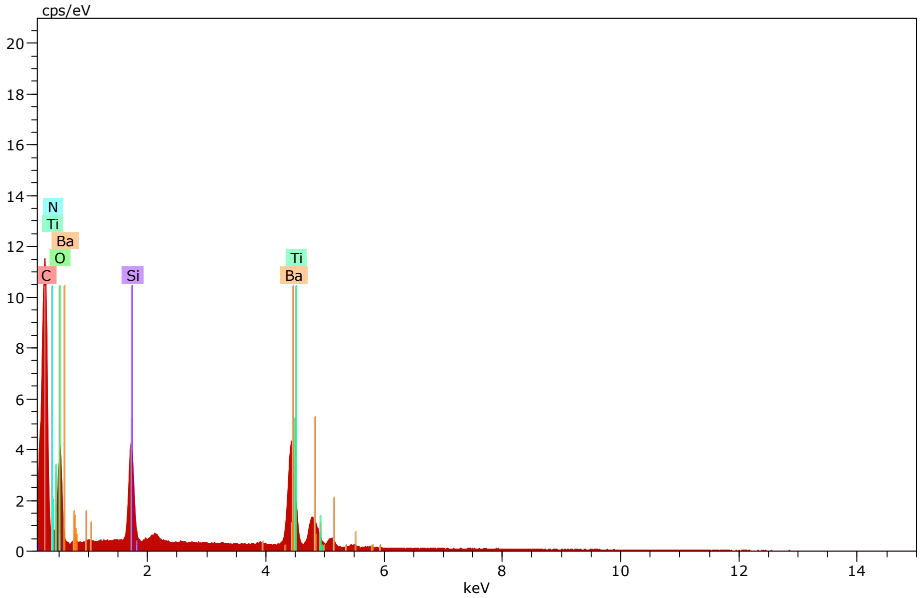


Figure SI 1d. EDX spectrum of synthesized $BaTiO_3$-g-GO.

Spectrum: Acquisition 9811

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]	K fact.	Z corr.	A corr.	F corr.
Ba	56	L-series	43.90	41.41	6.47	1.30	0.320	1.258	1.000	1.028
C	6	K-series	42.35	39.95	71.37	4.98	0.766	0.521	1.000	1.000
O	8	K-series	14.53	13.71	18.38	1.92	0.165	0.829	1.000	1.000
Si	14	K-series	5.24	4.94	3.78	0.25	0.028	1.726	1.000	1.008
Ti	22	K-series	0.00	0.00	0.00	0.00	0.000	0.000	1.000	1.083
N	7	K-series	0.00	0.00	0.00	0.00	0.000	0.000	1.000	1.000
		Total:	106.03	100.00	100.00					

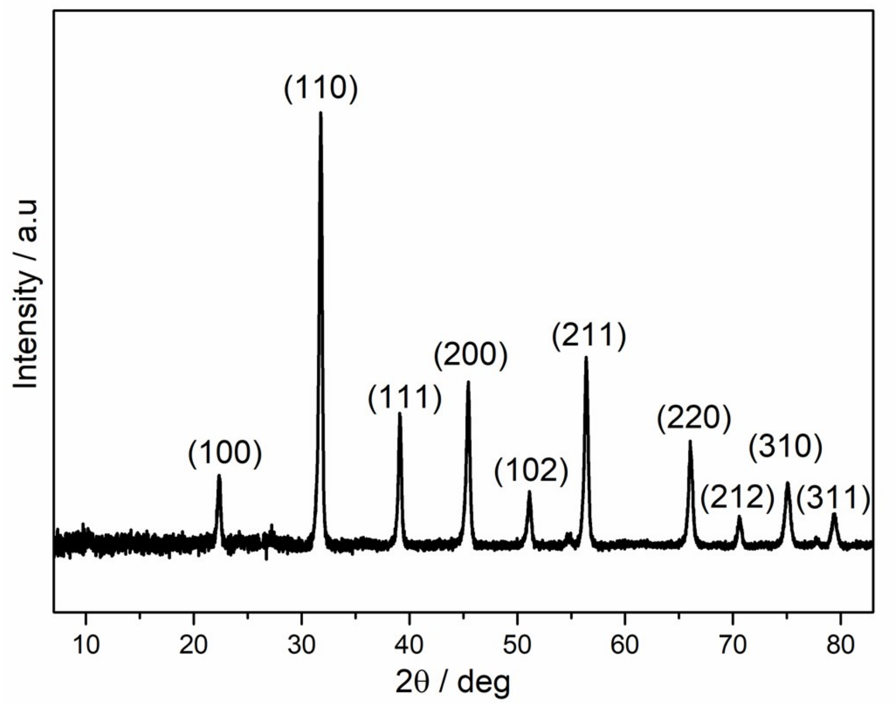


Figure SI 1e. XRD spectrum of $BaTiO_3$-g-GO

XRD spectrum of $BaTiO_3$-g-GO showed characteristic peaks of $BaTiO_3$. Since GO constitutes only 0.3 wt%, GO peaks are not visible in XRD. Diffraction peaks for $BaTiO_3$ nanoparticles were observed at 2θ 22.38º, 31.78º, 39.15º, 45.42º, 51.14º, 56.41º, 66.08º, 70.68º, 75.07º, and 79.42º and these peaks signify the Bragg reflections from the (100), (110), (111), (200), (102), (211), (220), (212), (310), and (311) planes correspondingly.[1] The obtained XRD pattern matches well with the standard XRD pattern of $BaTiO_3$ particle [JCPDS card no. 79-2264].

SEM images of Ba-TiO_3-g-GO

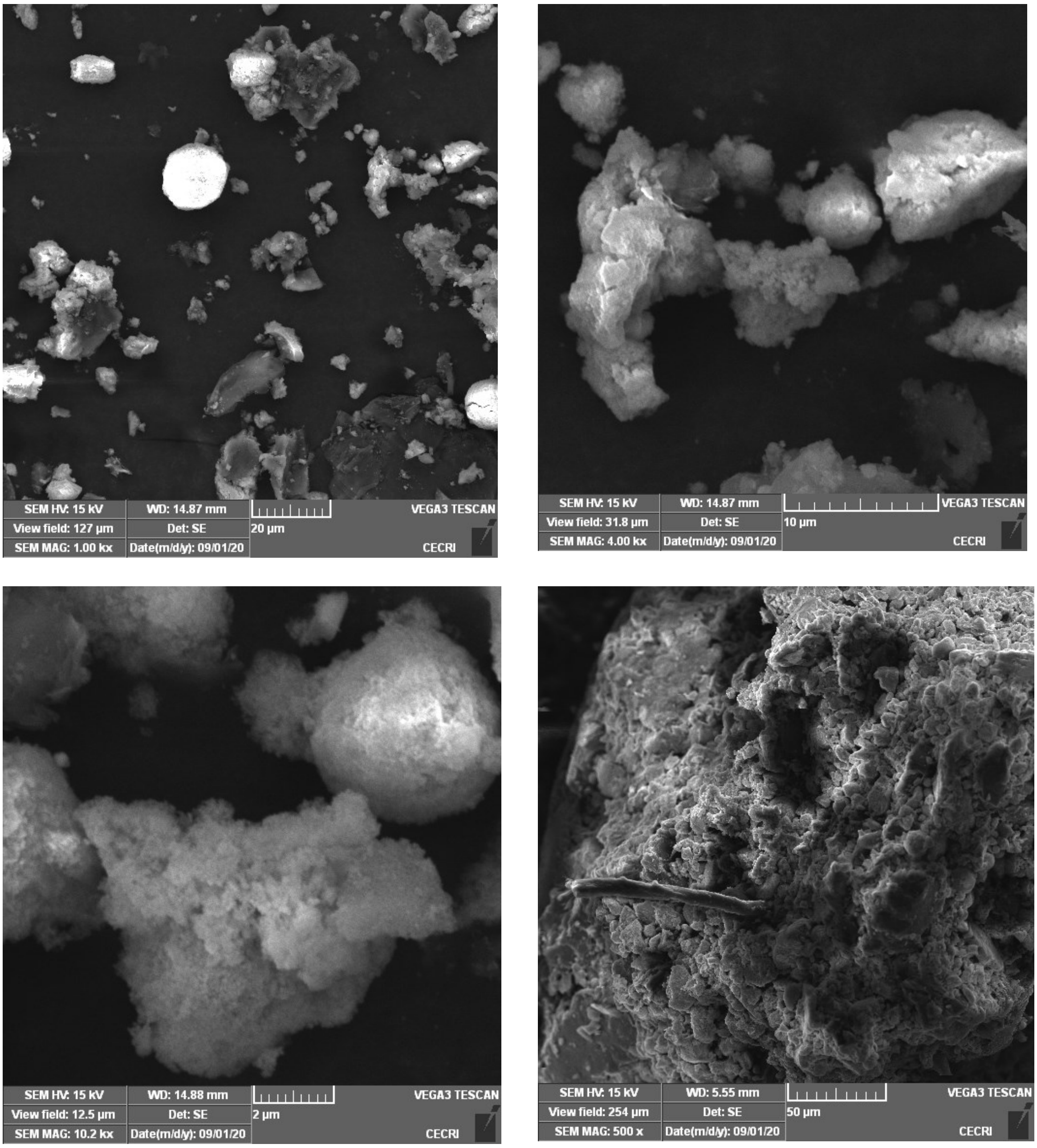


Figure SI 1f. SEM images of $BaTiO_3$-g-GO at different magnifications

XPS spectrum of synthesized $BaTiO_3$-g-GO

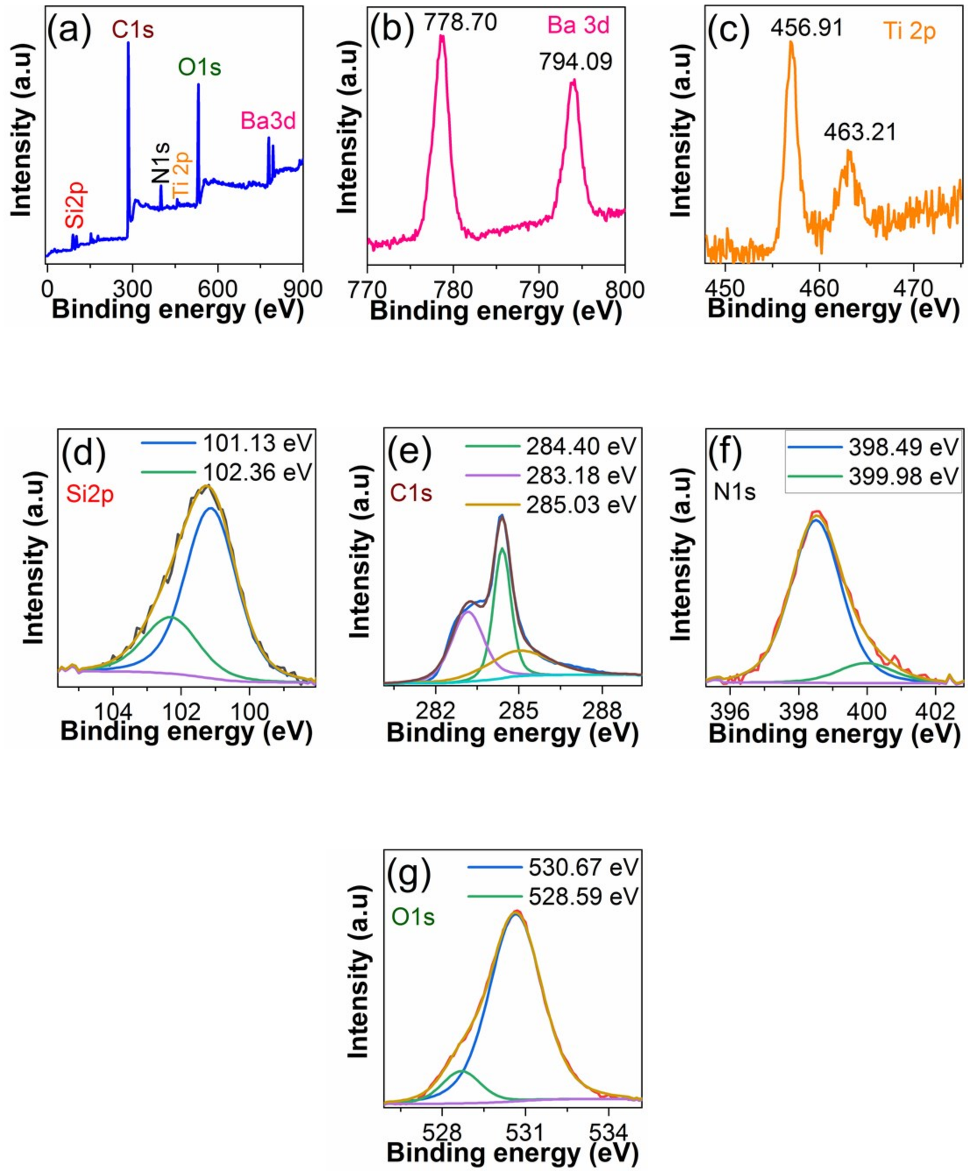


Figure SI 1g. XPS spectrum of the as synthesized $BaTiO_3$-g-GO a) Survey spectrum, b) Ba 3d spectra, c) Ti 2p spectra, d) Si 2p spectra, e) C 1s spectra, f) N 1s spectra and g) O 1s spectra.

The XPS survey spectrum shows evident peaks of C, O, N, Si, Ba, and Ti (Figure SI 1g-a) indicating the existence of $BaTiO_3$, linking APTS, and GO.

- The two peaks at 778.7 and 794.09 eV are ascribed to the splitting of Ba $3d_{5/2}$ and Ba $3d_{3/2}$ spin states correspondingly (Figure SI 1g-b).
- Two bands at 456.91 and 463.21 eV are ascribed to Ti $2p_{3/2}$ and Ti $2p_{1/2}$ respectively.
- Si 101.13, 102.36 eV corresponds to Si-O and SiO_2 respectively.

- C 1s 284.40 eV indicates the presence of C-C/C=C, 283.18 assigned to C-C/C-H and 285.03 eV to presence of C-O bond, all of which corresponds to GO.
- N 1s -398.49 eV attributed to N-H in amine, and 399.98 eV ascribed to N-C single bonds.
- 530.67 eV assigned to C-O bond, and 528.59 eV assigned to oxides (TiO, SiO).

All these results clearly indicate the existence of $BaTiO_3$-grafted graphene oxide interconnected via APTES linkage.

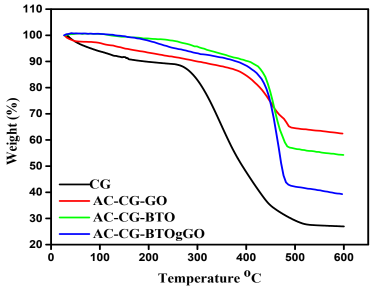


Figure SI 2. TG- curves for the coated membrane.

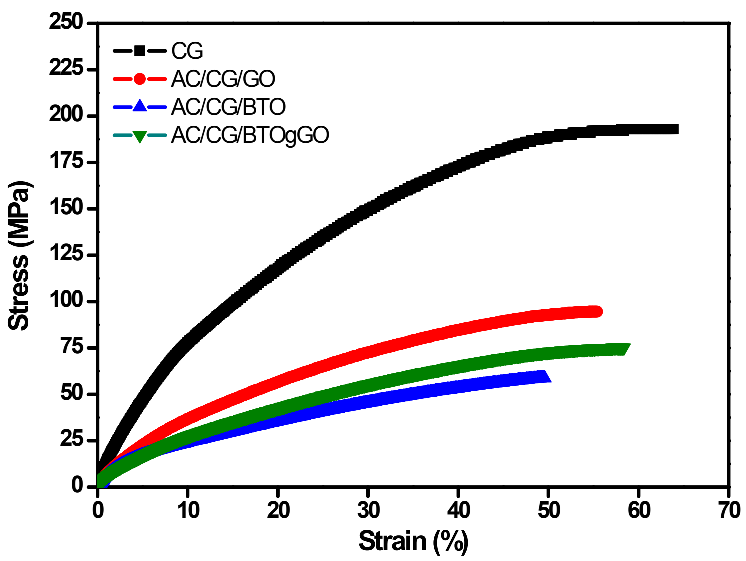


Figure SI 3. Stress- strain plot of Celgard 2320, AC/ GO, AC/BTO and AC/ BTO-g-GO coated trilayermembrane separators.

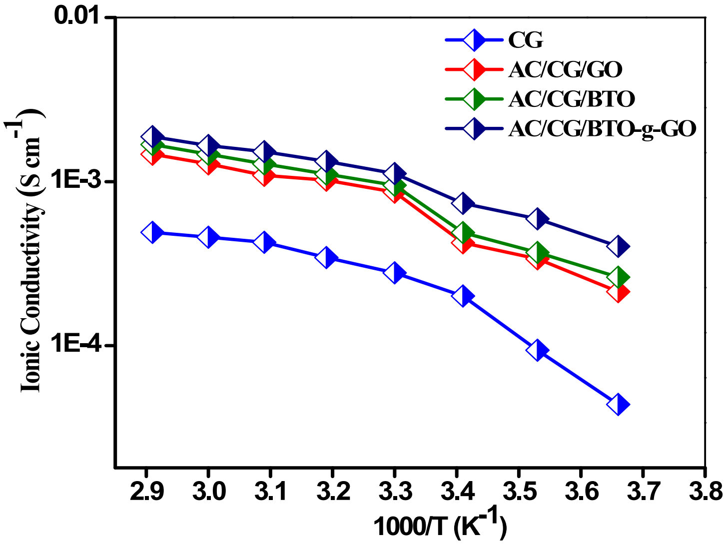
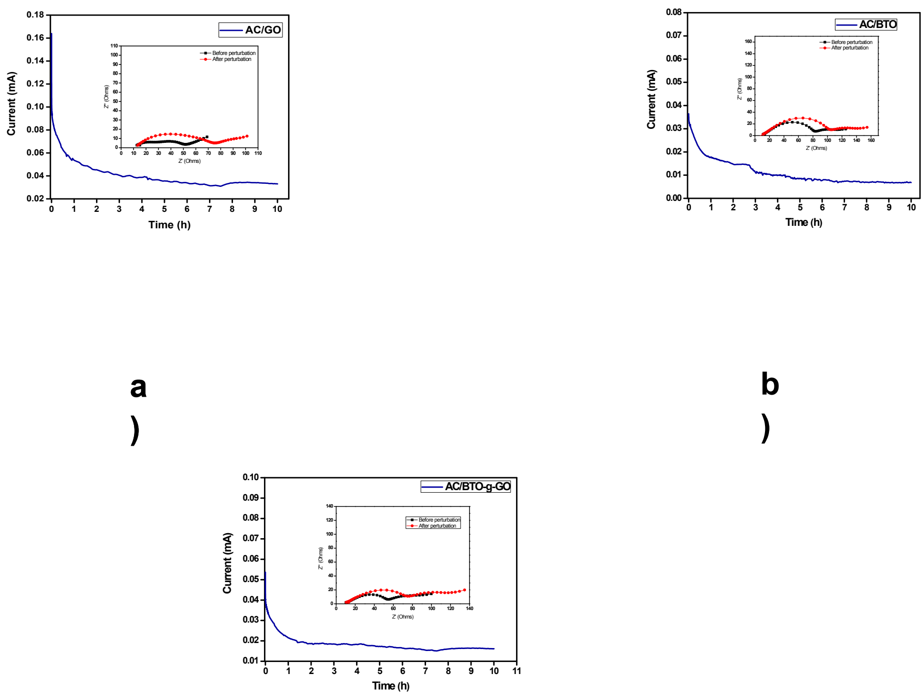


Figure SI 4. Variation of ionic conductivity as a function of inverse temperature.



a
)

b
)

c
)

Figure SI 5. Chronoamperometric curve for the Li-S cells with a)AC/ GO, b) AC/BTO and c) AC/ BTO-g-GO after perturbation. **Inset:** Impedance spectra of the cell before and after DC polarization at room temperature.

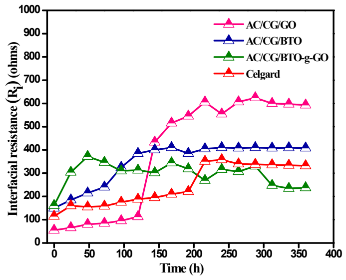


Figure SI 6. The variation of interfacial resistance as a function of time for Li/Separator/Li symmetric cells at room temperature.

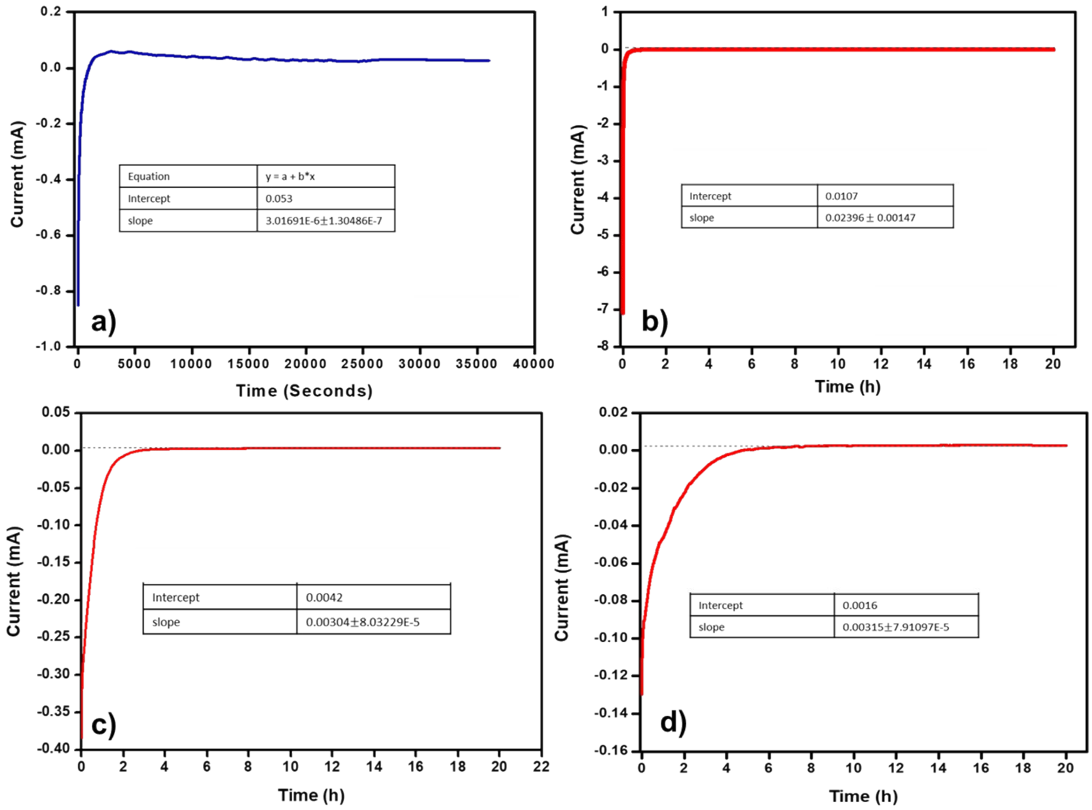
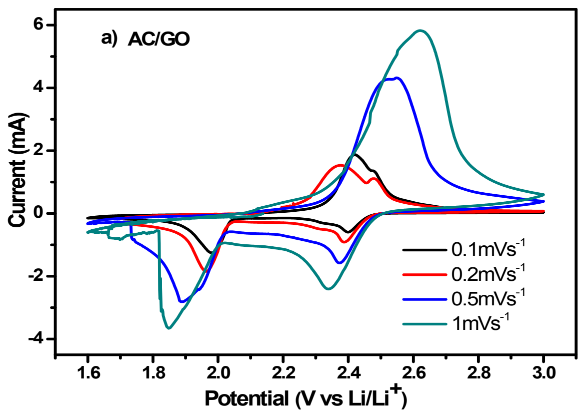
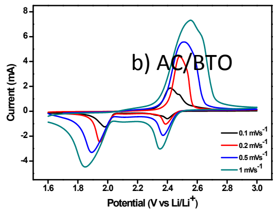


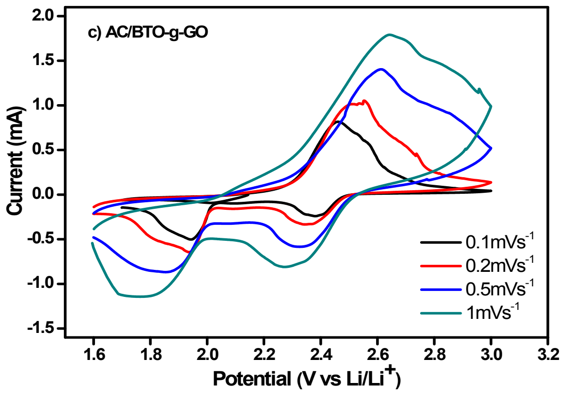
Figure SI 7. Current profile of Li-S cells with a) Celgard b) AC/GO c) AC/BTO d)AC/BTO-g-GO held at a constant potential of 2.3 V.





Peak	Diffusion coefficient (cm^2s^{-1})
2.4	5.1×10^{-5}
1.99	8.9×10^{-5}
2.4	3.02×10^{-6}
2.48	2.04×10^{-6}

Peak	Diffusion coefficient (cm^2s^{-1})
2.4	9.3×10^{-5}
1.99	1.02×10^{-6}
2.4	2.84×10^{-6}
2.48	2.6×10^{-6}



Peak	Diffusion coefficient (cm^2s^{-1})
2.4	5.31×10^{-4}
1.99	6.28×10^{-4}
2.4	1.47×10^{-5}
2.48	1.17×10^{-5}

Figure SI 8. The lithium-ion diffusion coefficients calculated for Li-S cells with a) AC/GO b) AC/BTO and d) AC/BTO-g-GO membranes.

Table 1. Comparison of permselective trilayer membranes properties with the present system

Sl. No	Sulfur content (wt%)	Mass loading of S electrode (mg/cm^2)	Thickness of the coating layer (µm)	Mass of the coating layer (mg/cm^2)	Initial discharge capacity (mAh/g)	Reversible discharge capacity (mAh/g)	No. of cycles	C rate	Degradation rate per cycle (%)	Reference
1	75	0.75	25	1.32	1067.7	804.4	100	0.2 C	1.3	2
2	80	2.5(areal loading)	35	1	1110.4	801.6	300	0.5	NA	3
3	60	1.4	8	0.01	1020	709	100	0.2	0.3	4
4	63	1.5	20	0.12	920	NA	100	0.1	0.49 to 0.23	5
5	60	1	25	0.5	836	610	200	0.1	0.1	6
6	72	0.72	47	0.8	1350	620	100	0.1	2.20	7
7	80	1	NA	NA	1045	628	50	0.05	1.6	8
8	42	1	42	NA	1287	807.8	100	0.2	1.60	9
9	80	0.7	20	0.825	1382	924	200	0.1	1.4	10
10	70	1.7	35	0.9	1382	1015	200	0.2	0.1	11
11	70	4	25	0.8	1450	833.3	100	0.1	0.6	12

Supporting References

1 S. Nayak, B. Sahoo, T. K. Chaki and D. Khastgir, *RSC Adv.*, 2014, **4**, 1212–1224.

2 R. Song, R. Fang, L. Wen, Y. Shi, S. Wang and F. Li, *J. Power Sources*, 2016, **301**, 179–186.

3 G. Ma, F. Huang, Z. Wen, Q. Wang, X. Hong, J. Jin and X. Wu, *J. Mater. Chem. A*, 2016, **4**, 16968–16974.

4 C. H. Chang, S. H. Chung and A. Manthiram, *J. Mater. Chem. A*, 2015, **3**, 18829–18834.

5 J. Q. Huang, T. Z. Zhuang, Q. Zhang, H. J. Peng, C. M. Chen and F. Wei, *ACS Nano*, 2015, **9**, 3002–3011.

6 H. Yao, K. Yan, W. Li, G. Zheng, D. Kong, Z. W. Seh, V. K. Narasimhan, Z. Liang and Y. Cui, *Energy Environ. Sci.*, 2014, **7**, 3381–3390.

7 M. Raja, S. Suriyakumar, N. Angulakshmi and A. Manuel Stephan, *Inorg. Chem. Front.*, 2017, **4**, 1013–1021.

8 X. Ou, Y. Yu, R. Wu, A. Tyagi, M. Zhuang, Y. Ding, I. H. Abidi, H. Wu, F. Wang and Z. Luo, *ACS Appl. Mater. Interfaces*, 2018, **10**, 5534–5542.

9 Q. Xu, G. C. Hu, H. L. Bi and H. F. Xiang, *Ionics (Kiel).*, 2015, **21**, 981–986.

10 W. Ahn, S. N. Lim, D. U. Lee, K. B. Kim, Z. Chen and S. H. Yeon, *J. Mater. Chem. A*, 2015, **3**, 9461–9467.

11 J. Balach, T. Jaumann, M. Klose, S. Oswald, J. Eckert and L. Giebeler, *J. Phys. Chem. C*, 2015, **119**, 4580–4587.

12 The present work.