

Supplementary Information for:

**UCST Polymer functionalized Graphene Oxide Membrane with Reversible Thermal Cut-off Mechanism for Safer Lithium-ion Batteries**

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## **I. Materials and Methods**

### **Graphene oxide (GO)**

GO was synthesized from flake graphite (Asbury Carbons, 230U Grade, High Carbon Natural Graphite 99+) by a modified Hummers method. The graphite powder (2.0 g) was pre-oxidized by stirring it into a concentrated  $\text{H}_2\text{SO}_4$  (20 mL) solution in which  $\text{K}_2\text{S}_2\text{O}_8$  (1.0 g) and  $\text{P}_2\text{O}_5$  (1.0 g) were completely dissolved at  $80^\circ\text{C}$ . The mixture, in a beaker, was kept at  $80^\circ\text{C}$  for 4.5 h using an oil bath. After the mixture was cooled and diluted with 1 L of DDI (distilled deionized) water, the pretreated product was filtered with a Nylon membrane filter (47 mm diameter,  $0.2\ \mu\text{m}$  pore size, Milipore) and washed on the filter until the pH of filtrate water became neutral. The shiny, dark-gray, preoxidized graphite was dried in air overnight. Then it was dispersed by stirring into chilled  $\text{H}_2\text{SO}_4$  (75 mL) in an Erlenmeyer flask in an ice bath.  $\text{KMnO}_4$  (10 g) was added slowly with stirring to keep the temperature of reaction mixture below  $20^\circ\text{C}$ . The resulting thick, dark green paste was allowed to react at  $35^\circ\text{C}$  for 2 h followed by addition of DDI water (160 mL) to form a dark brown solution. To avoid over-flow of the mixture due to rapid temperature rise with foaming by water addition, the flask was chilled in an ice bath and water was added in  $\sim 5$  mL aliquots with close monitoring of temperature (kept below  $50^\circ\text{C}$ ). After additional stirring for 2 h, the dark brownish solution was further diluted with distilled water (500 mL), and  $\text{H}_2\text{O}_2$  (30%, 8.3 mL) was added slowly. The color of the mixture turned bright yellow. The mixture was allowed to settle overnight. The supernatant was decanted and the remaining product was repeatedly centrifuged and washed with DDI water until the pH of the solution became neutral. (At this stage, the Mn concentration in the supernatant was below 0.1 ppm by AAS). Then, the obtained product was diluted to make a  $\sim 0.5\%$  w/w aqueous dispersion for storage.

### **4-hydroxyethylphenyl functionalized graphene oxide (GO-OH)**

GO (0.50 g, 5 mmol) was homogeneously suspended in 250 mL DDI water. 4-aminophenethyl alcohol (6.3 g, 50 mmol), isopentyl nitrite (75 mL, 0.5 mol) were added into the GO suspension. The reactor with condenser was filled with nitrogen, heated at  $60^\circ\text{C}$ , and refluxed for 3 h. The reaction mixture was filtered over a Nylon membrane (47 mm diameter,  $0.2\ \mu\text{m}$  pore size), washed with acetone (250 mL), DMF (250 mL), water (250 mL), and acetone (250 mL). This process was repeated several times until the impurities were completely removed. Finally, the

mixture was washed with a diethyl ether (250 mL) and dried overnight in a vacuum oven at 60 °C.

### **2-Bromo-2-methylpropanoate-4-methylphenethyl functionalized graphene oxide (GO-Br)**

GO-OH (220 mg, 2.2 mmol) was dispersed in a mixture of dry THF (50 mL) and DMF (150 mL) by sonication for 1 hour. Triethylamine (61.31 mL, 440 mmol) was added in the reaction, followed by the dropwise addition of  $\alpha$ -bromoisobutyryl bromide (5.5 mL, 44 mmol) in ice bath for 1 h. The mixture was allowed to stir for 48 h at room temperature. The reaction mixture was filtered over a Nylon membrane (47 mm diameter, 0.2  $\mu$ m pore size), washed with acetone (250 mL), THF (250 mL), DMF (250 mL), and DDI water (250 mL). This process was repeated several times until the impurities were completely removed. Finally, the product was washed with a diethyl ether (250 mL) and dried overnight in a vacuum oven at 60 °C.

An elemental analysis determined the elemental weight fraction of C, H, N, O of GO-Br to be 64.48%, 3.63%, 2.70%, and 12.97%, respectively. The content of Br is estimated to be 16.22% based on a total weight of 100%.

### **GO-PMABS**

GO-Br (0.10 g) and 3-(N-2-methacryloyloxyethyl-N,N-dimethyl)ammonatobutanesulfonate (MABS, 15g, 53.5 mmol) were mixed in 40 mL DDI water and 160 mL MeOH at room temperature and deoxygenated by passing a continuous stream of dry argon through the solution while stirring for 30mins. 2,2'-Dipyridyl (420 mg, 2.7mmol) , CuCl (106 mg, 1.08 mmol), and CuCl<sub>2</sub> (15 mg, 0.10 mmol) were added to this solution under the protection of argon flow. The mixture was then stirred while deoxygenating with a stream of dry argon for another 30min. The polymerization started as soon as the catalysts were in.

The polymerization was finally stopped at 72 h by exposing the mixture to air. GO-PMABS72h was filtered over a Nylon membrane (47 mm diameter, 0.2  $\mu$ m pore size), washed by hot water several times to remove free polymers which could be physically adhered to the surface of GO-PMABS72h. The resulting GO-PMABS72h was dried under vacuum at 60°C for 24 h.

The molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) of the PMABS were obtained using the free polymers formed from the sacrificial initiator, ethyl 2-bromoisobutyrate (EBiB), under the same reaction condition. It is generally believed that the free polymer initiated by the sacrificial initiator in solution has almost identical molecular weights to those formed from the solid support. Two polymerization times, 36 hours and 72 hours, were used for comparison. A multi-angle light scattering coupled to size-exclusion chromatography (Sec-Mals) with polystyrene (PS) standards were used in the determination. The sample with 72 hours polymerization time has higher molecular weight (230,000 g/mol) than the one with 36 hours does (153,000 g/mol), as expected. The two samples both had relatively broad MWD ( $M_w/M_n = 1.62$  for the PMABS-36h, and 1.48 for the PMABS-72h), consistent with the previous studies of the polymerization process in methanol/water solution.

### **PMABS72h on glass fiber membrane (GF-P)**

The composite membranes were prepared by casting the 10wt % PMABS72h water solution on the glass fiber membrane at about 40°C and dried under vacuum at 100°C for 24h.

## **II. Characterization**

The morphology of as-prepared samples was investigated using Hitachi S-4800-II field emission scanning electron microscopy (FE-SEM), JOEL 2100F field emission transmission electron microscopy (FE-TEM), and Hitachi HD-2300A FE-STEM operated at 200 kV with energy dispersive spectroscopy (EDS) detectors. X-ray photoelectron spectroscopy (XPS) was performed using an Omicron ESCA Probe equipped with an electron flood gun. The  $AlK_{\alpha}$  radiation (1486.6 eV) was used as an excitation source and the binding energy scale was calibrated with respect to adventitious carbon (C1s). Thermogravimetric analysis (TGA, Mettler Toledo, TGA/SDTA851e) was performed under nitrogen. The samples were heated to 100°C and held at 100°C for 10 min to remove any volatiles and adsorbed water. Then the temperature was ramped to 800°C at the rate of 10°C min<sup>-1</sup> in flowing nitrogen. Elemental analysis was performed by Robertson microlit laboratories.

UV-vis absorbance spectra were collected using a HP (Agilent) 8452 diode array spectrophotometer. The molecular weight was determined using the SEC-MALS-QELS system

is composed of an Agilent 1260 series HPLC for size exclusion chromatography followed by a Wyatt DAWN HELEOS II multi-angle static light scattering detector, a Wyatt QELS dynamic light scattering detector, and a Wyatt T-rEx differential refractive index detector. The measurement followed the literature procedure.<sup>1</sup> 200mM NaCl aqueous solution was used as an eluent at a rate of 0.8 mL min<sup>-1</sup>. The specific refractive index increments (dn/dc) of PMABS was determined as 0.12 mL g<sup>-1</sup>. Both of the UV-vis and SEC-MALS measurements were performed in Keck Biophysics Facility, northwestern university.

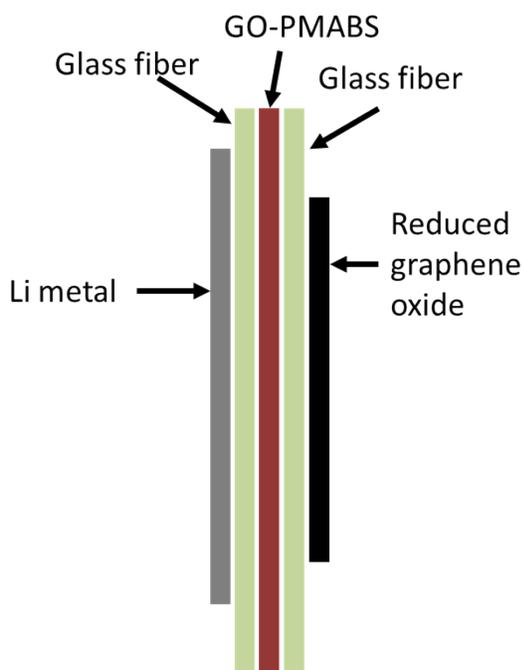
Quartz Crystal Microbalance (QCM) measurements were conducted using a CHK-100 crystal holder (Inficon, East Syracuse, NY) and a 250 B/C network analyzer (Saunders and Associates, Phoenix, AZ) to record the frequency. To characterize the polymer swelling in the electrolyte, free PMABS(72h) was spin-cast from water onto the surface of an AT-cut, 5 MHz quartz crystal disc (1 in. diameter) with chrome electrodes (Inficon, East Syracuse, NY). First, the crystal resonance frequency was measured in air before and after spin-casting at three harmonics ( $n=1$ , 5 MHz;  $n=3$ , 15 MHz; and  $n=5$ , 25 MHz). Subsequently, the QCM crystal holder was placed vertically in a sealed container held in an oil bath set at 25 °C. After the container was purged of air with nitrogen gas, the electrolyte was Cannula transferred into it to prevent water contamination. Nitrogen was flowed over the electrolyte for the remainder of the experiment.

After the polymer-coated crystal was fully submersed in the electrolyte, shifts in the crystal resonance frequency ( $\Delta f_{p,25}$ ) were measured at all three harmonics for 45 min at 25 °C. Next, the temperature of the oil bath was increased to 50 °C. The bath took approximately 1 h to reach the higher temperature, and then frequency shifts ( $\Delta f_{p,50}$ ) were monitored for another h as the bath was held at 50 °C. All frequency shifts were referenced to the crystal resonance in air before spin-casting.

To correct for out the effects of liquid loading and temperature on the frequency shifts, the frequency shifts due to submersion of an uncoated crystal into the electrolyte at 25 ( $\Delta f_{b,25}$ ) and 50 °C ( $\Delta f_{b,50}$ ) were similarly determined. Frequency shifts can be converted to an areal mass change ( $\Delta M_A$ ) using the Sauerbrey relation,<sup>2</sup> which states that  $\Delta f \sim -n\Delta M_A$ , provided that these shifts are subtracted out from the total shift induced by submersing the polymer layer in the electrolyte.<sup>3,4</sup>

## Electrochemical Test

Electrochemical measurements were carried out using two-electrode coin cells with Li metal as the counter electrode, in an assembly shown below.



Microporous glass-fiber membrane (Whatman) was used as separator, and an Al foil was employed to connect the composite papers to external leads. The electrolyte consisted of 1 M  $\text{LiPF}_6$  in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (3:7, v/v). The coin cells for EIS measurements used one piece of GO-PMABS72h membrane in addition to GF as the separator. The galvanostatic measurements used two pieces of GO-PMABS72h sandwiched between two pieces of glass fiber as the separator.

The cells were assembled in an argon-filled glove

box, and galvanostatic measurements were conducted with a BT2000 Potentiostat/Galvanostat system (Arbin Instruments) at various current densities, over the voltage range of 0.02-1.5 V vs  $\text{Li/Li}^+$ . Cyclic voltammograms (CV) were recorded over the same voltage range at a scan rate of  $0.01 \text{ mVs}^{-1}$ . Electrochemical impedance spectroscopy (EIS) measurements were conducted using a Solartron 1260 impedance analyzer coupled with a Solartron 1286 electrochemical interface by applying an AC voltage of 10 mV amplitude and DC open circuit voltage (OCV) in the frequency range of 1 MHz-0.01 Hz at room temperature.

The temperature-dependent galvanostatic measurements used a constant current of 200 mA/g. An empty beaker was heated to  $80^\circ\text{C}$  in oil bath. The coin cells were put in the heated beaker during the cycle. The cell was in contact with the bottom of the beaker to ensure the desired temperature. The EIS at  $60^\circ\text{C}$  was measured in a similar way.

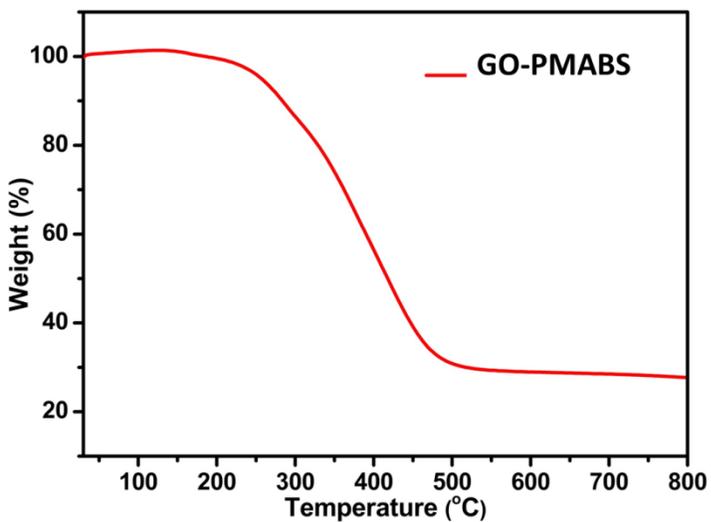


Figure S1a. TGA curve of GO-PMABS collected in N<sub>2</sub>.

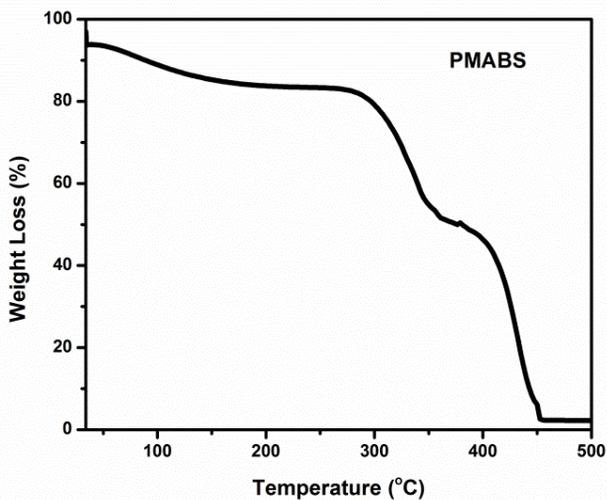


Figure S1b. TG curve of free PMABS as prepared.

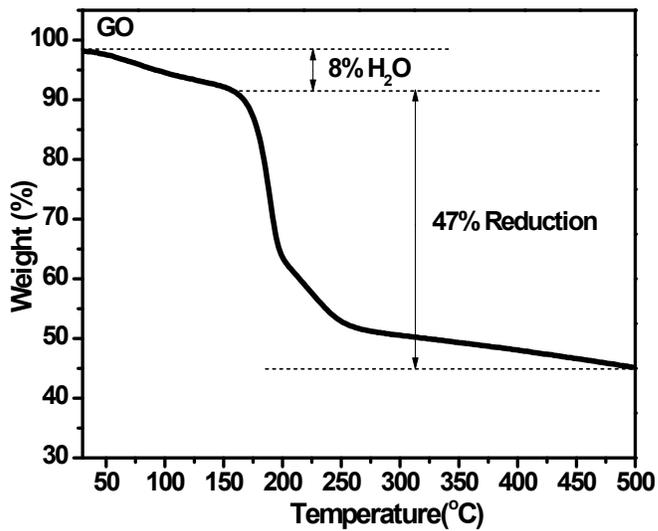
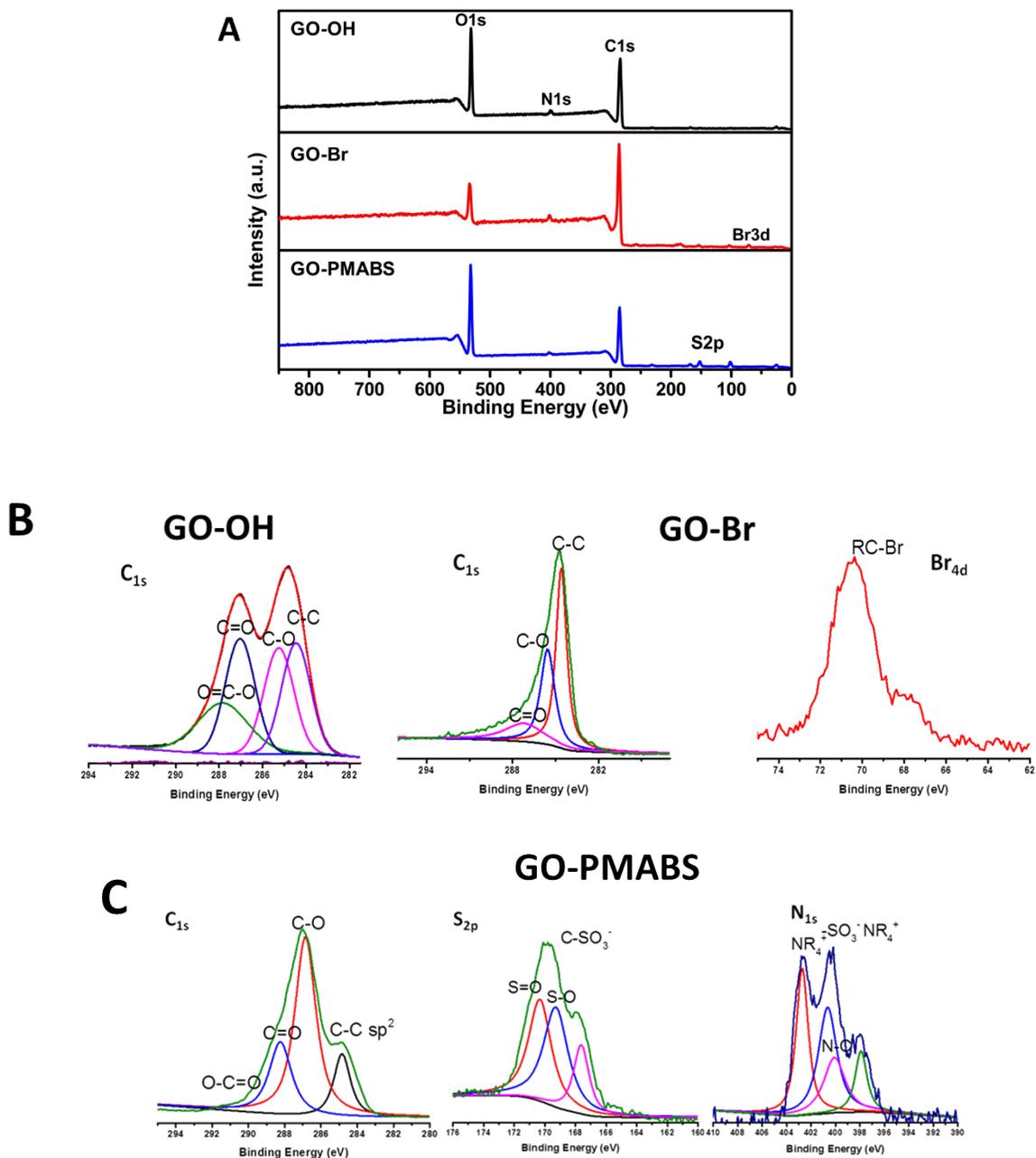
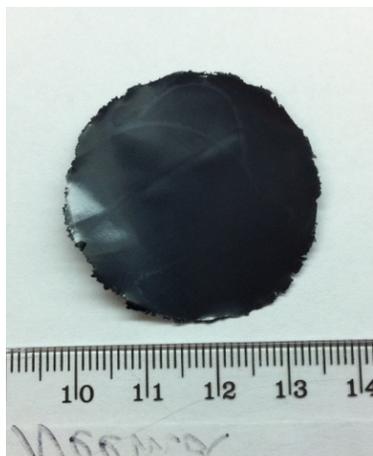


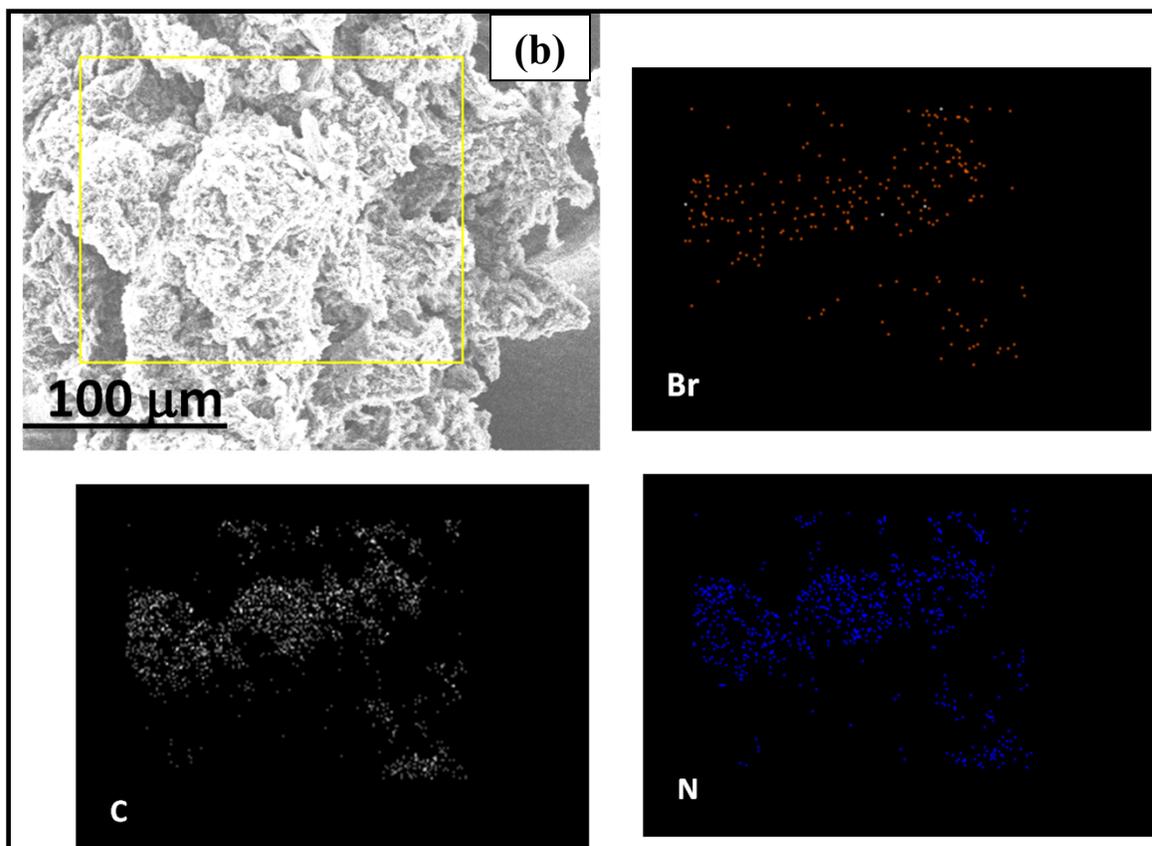
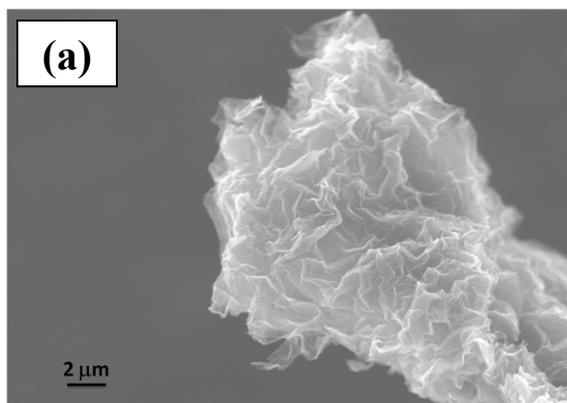
Fig.S1(c) TG curve of graphene oxide paper



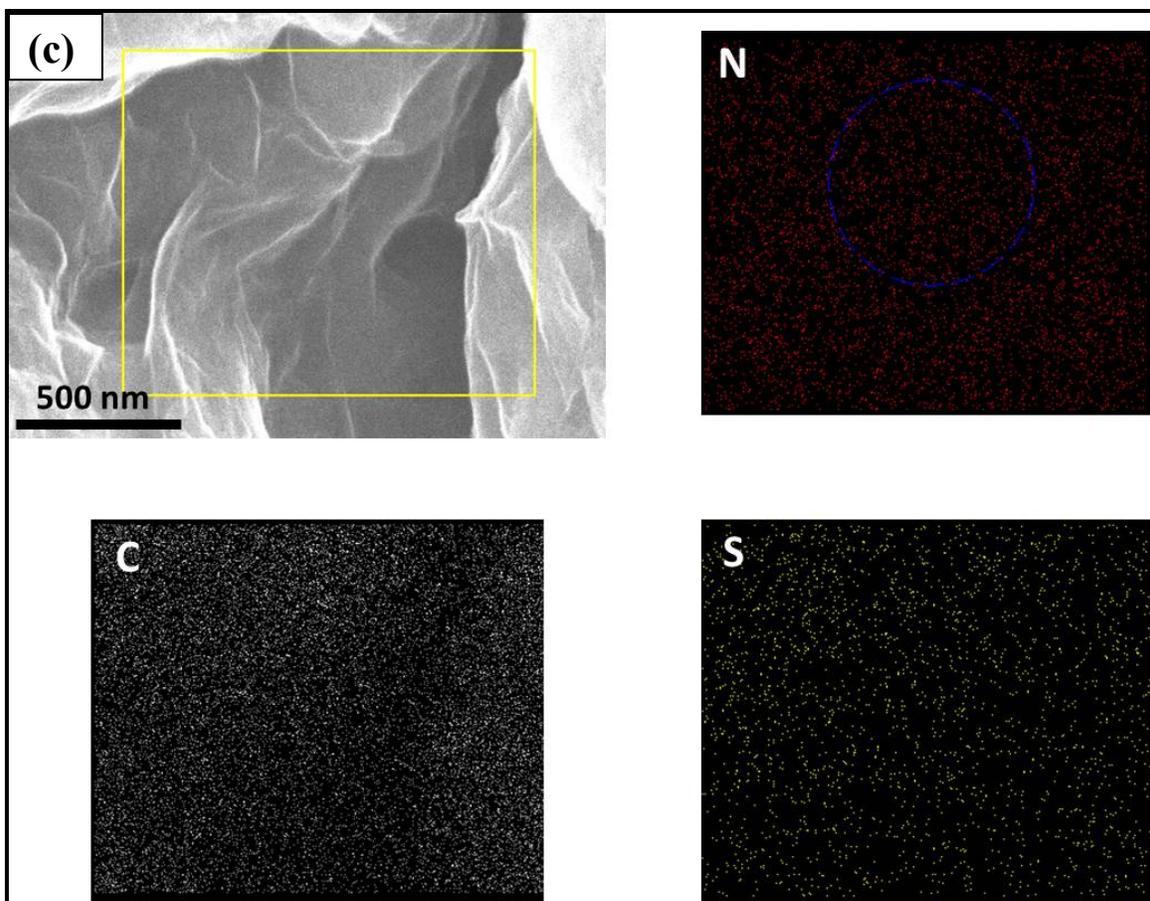
**Figure S2.** (a) XPS survey spectra of GO-OH, GO-Br, and GO-PMABS. (b) C1s spectrum of GO-OH, and C1s and Br4d spectra of GO-Br. (c) C1s, S2p, and N1s spectra of GO-PMABS.



**Figure S3.** A GO-PMABS membrane as prepared.

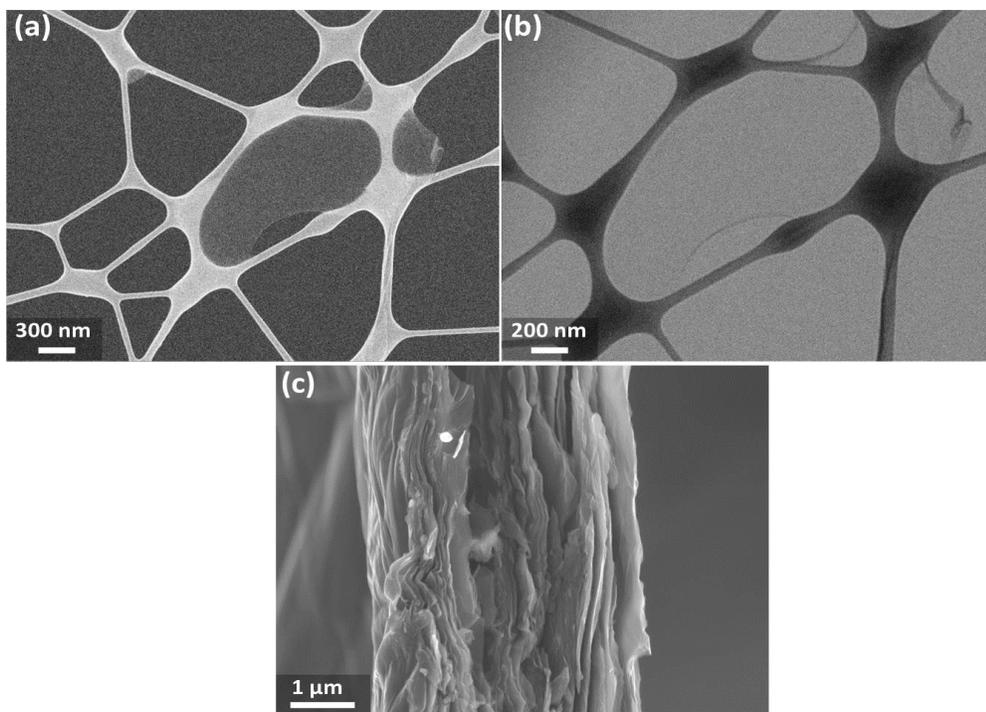


(b)

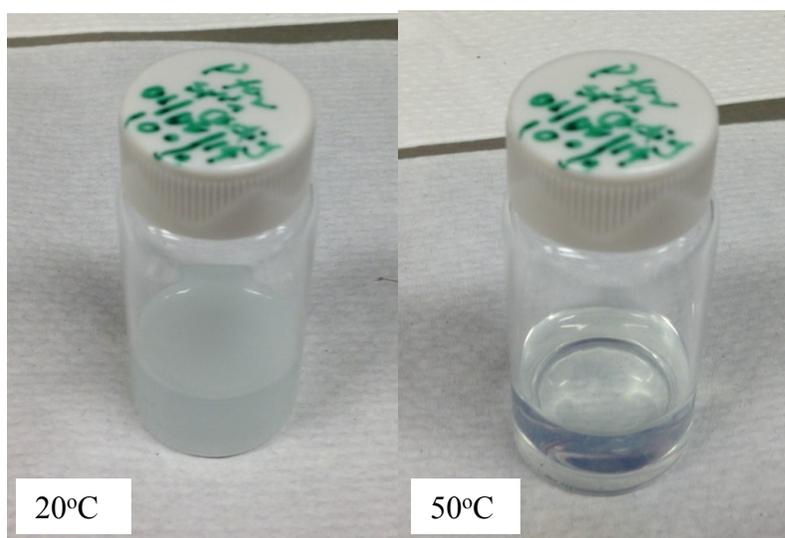


(c)

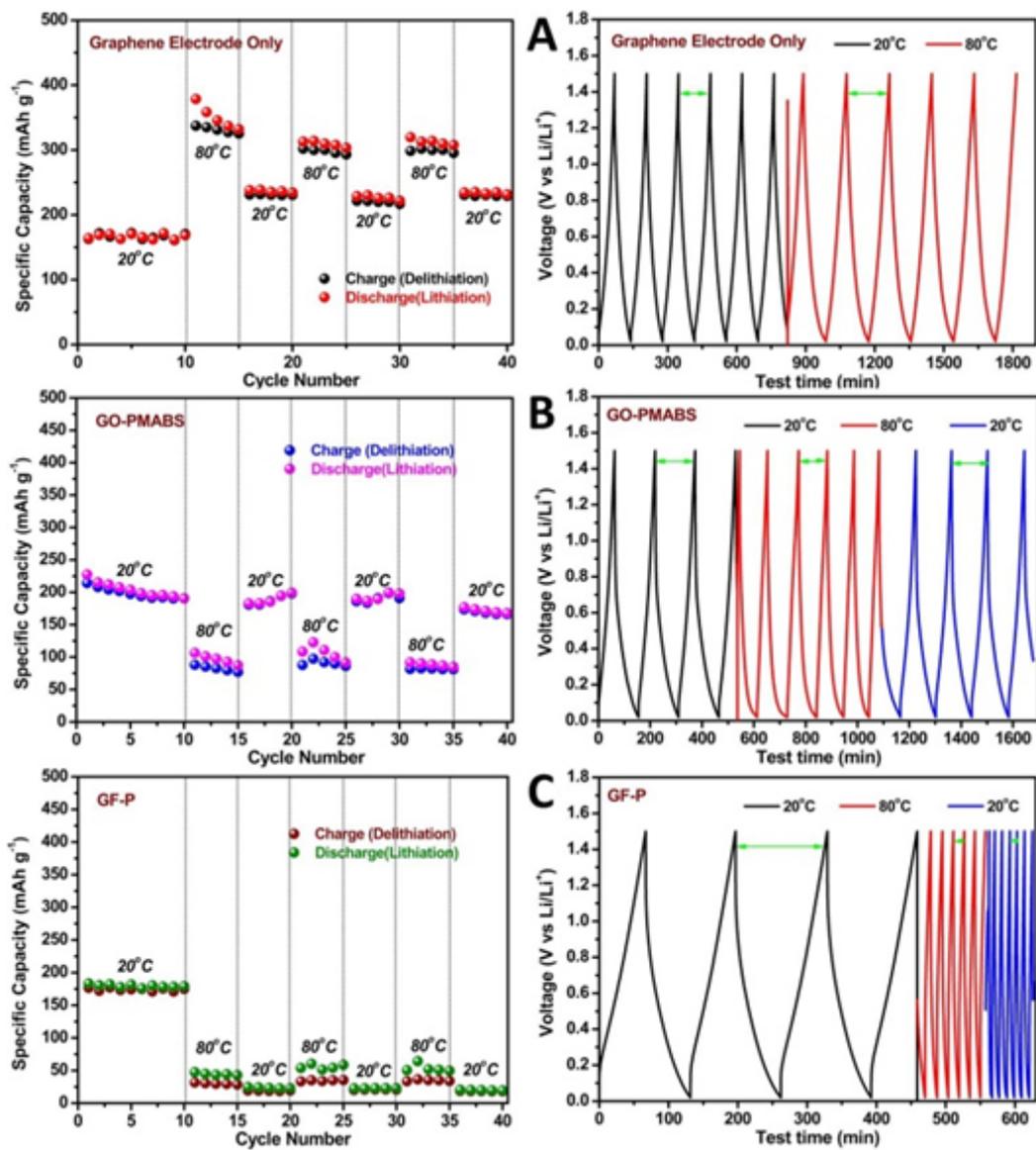
**Figure S4** (a) SEM image of GO-Br, (b) SEM and EDX spectra of GO-Br, and (c) SEM and EDX spectra of a GO-PMABS membrane.



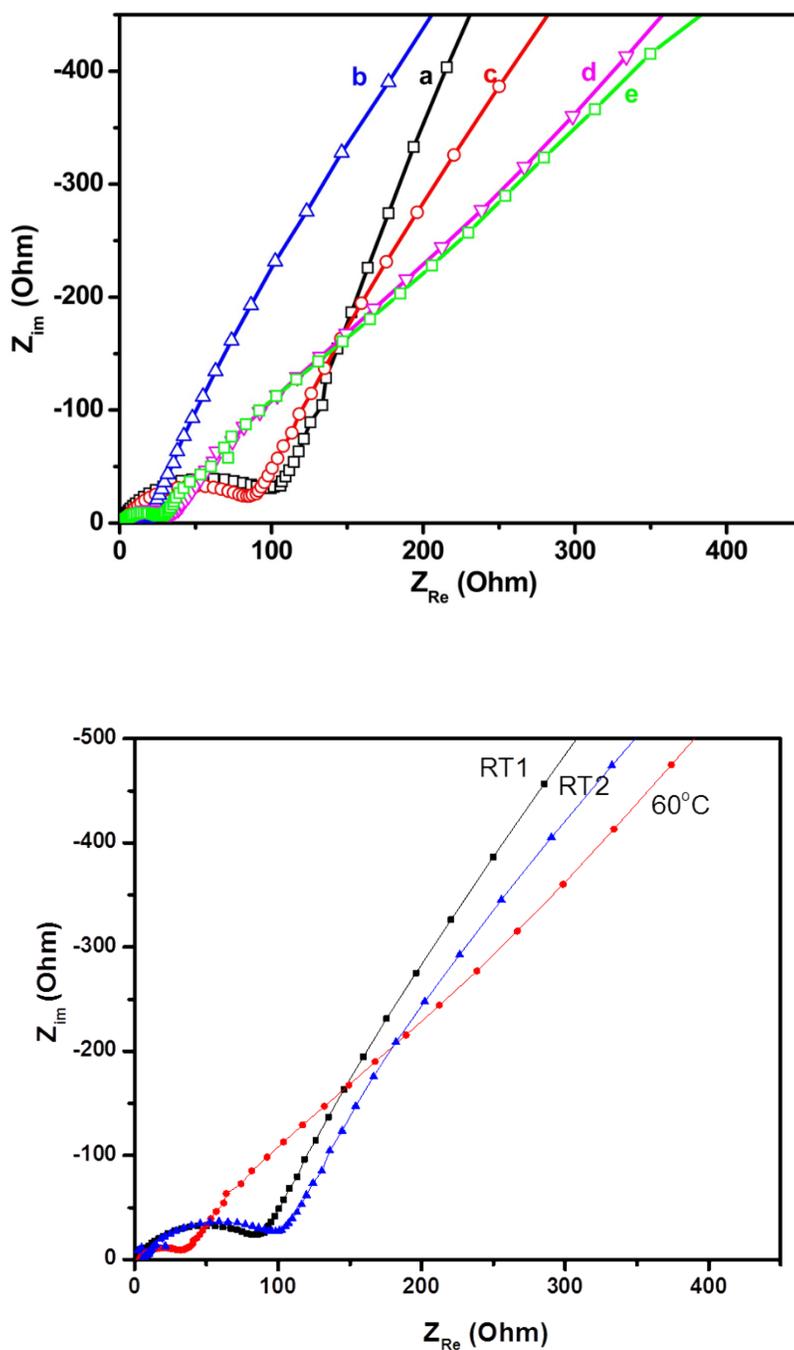
**Figure S5.** a) and b) TEM images of a single graphene oxide sheet, and c) Cross-sectional SEM image of the thermal reduced graphene paper anode (about 5.2μm thick). All the electrochemical analysis in the paper used the graphene paper anode with about the same thickness.



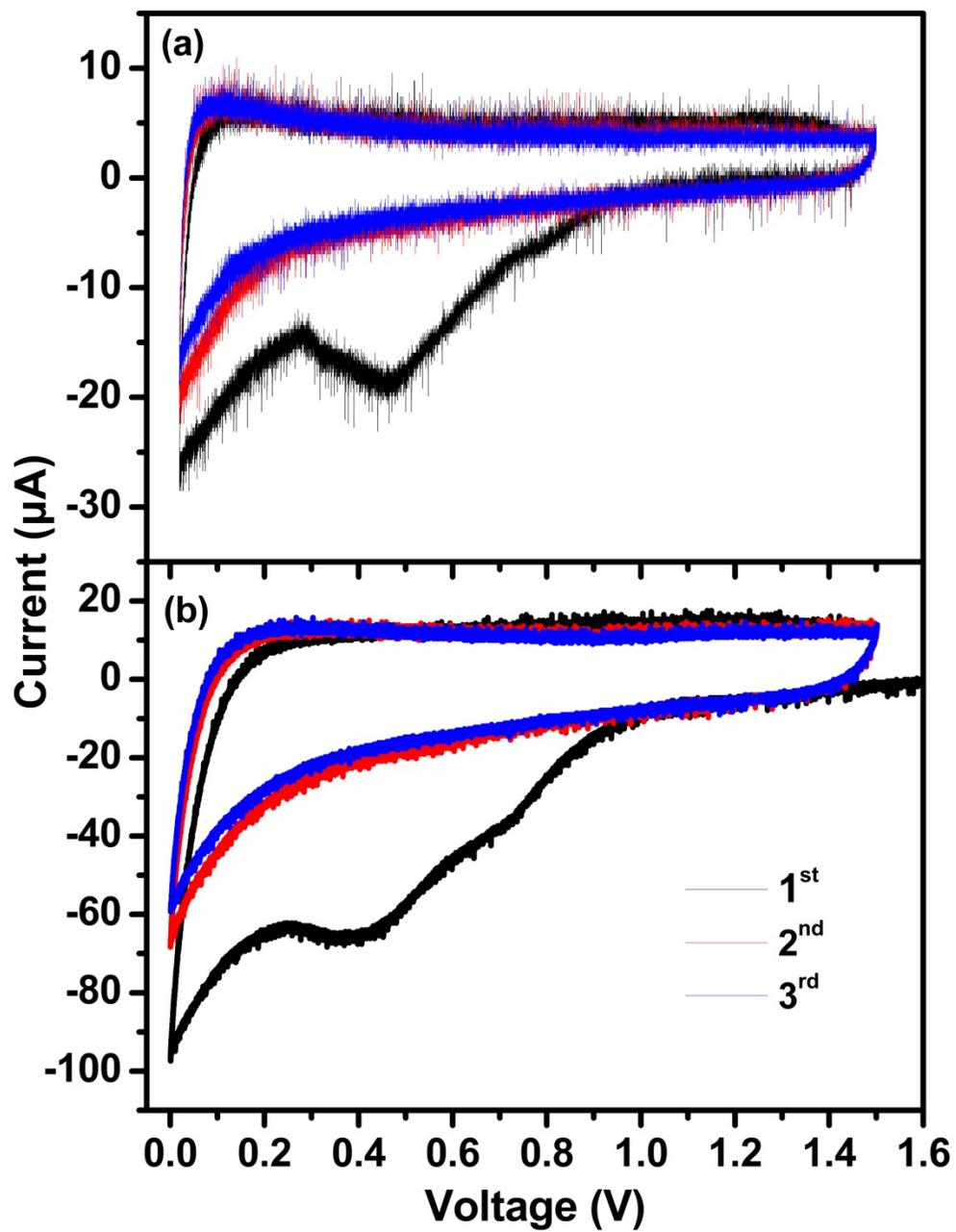
**Figure S6** 10wt% of PMABS in water at 20°C and 50°C.



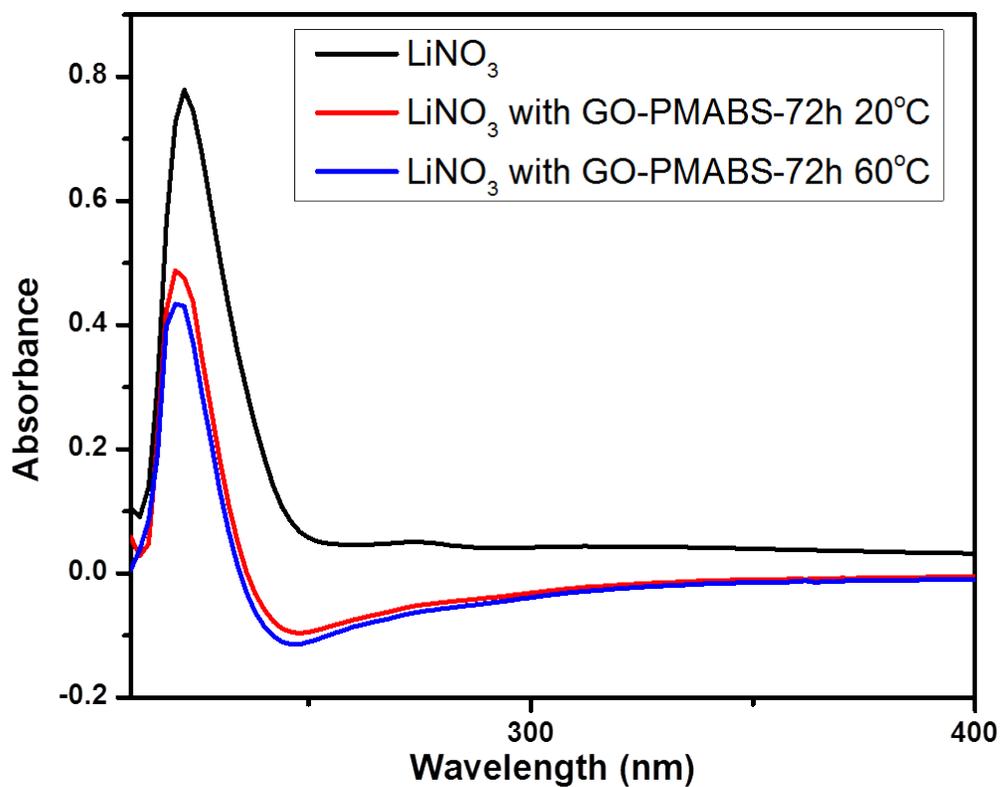
**Figure S7.** Specific charge capacity (mAh g<sup>-1</sup> graphene electrode) of Li metal-graphene paper cells, evaluated at 20 or 80°C. (A). Separator membrane without GO-PMABS. (B). Separator with GO-PMABS; and (C) Separator with GF-P, PMABS-impregnated onto glass fiber.



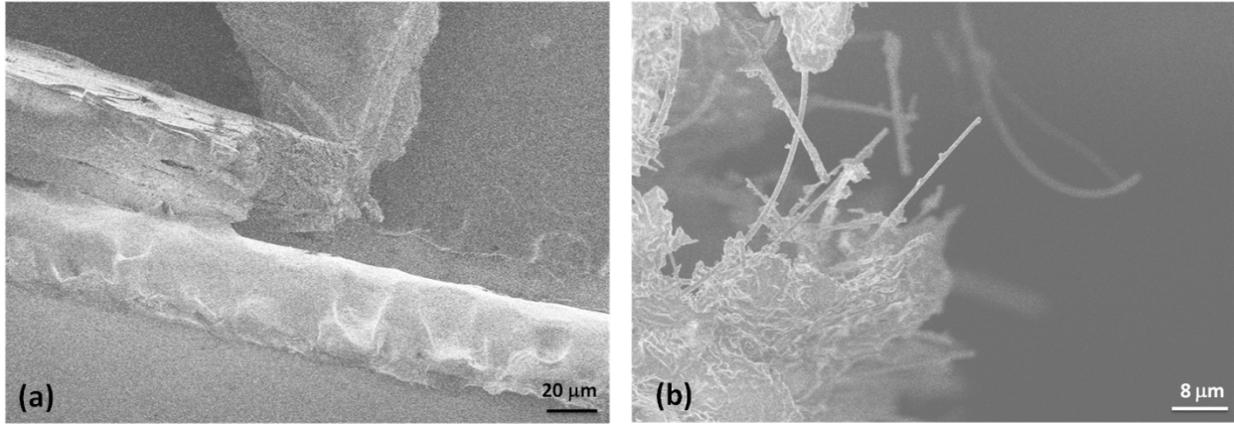
**Figure S8.** Nyquist plots of reduced graphene oxide paper anode and separator assembly. (A) Separator without GO-PMABS at (a) room temperature and (b) 60°C, and separator with GO-PMABS at (c) room temperature, (d) 60°C, and (e) 80°C. (B) Separator with GO-PMABS, first at room temperature (RT1), then at 60°C, then returned to room temperature (RT2).



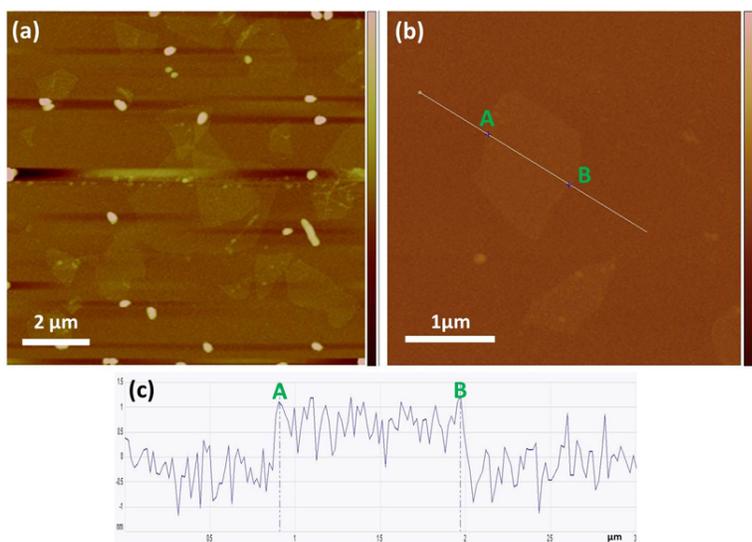
**Figure S9.** CV curves of reduced graphene oxide in the cell using a separator without (a) and with (b) GO-PMABS.



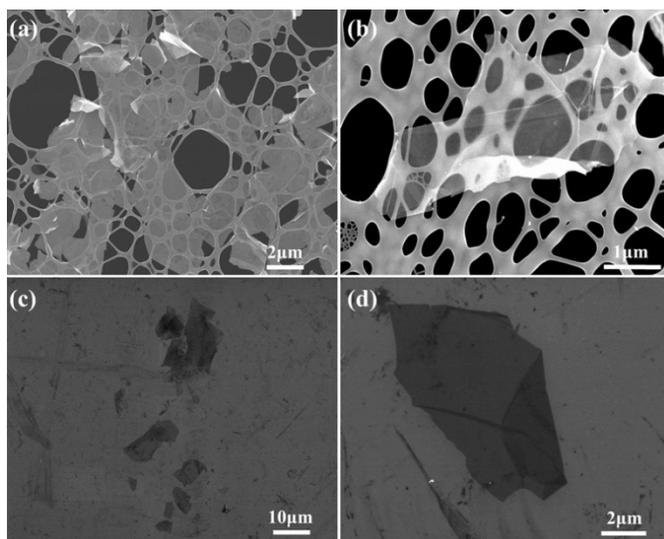
**Figure S10.** UV-vis spectra of LiNO<sub>3</sub> solution (black curve) only, LiNO<sub>3</sub> solution with GO-PMABS membranes at room temperature (red curve), and LiNO<sub>3</sub> solution with GO-PMABS at 60°C (blue curve).



**Figure S11.** The SEM images of a) cross section of GF-PMABS and b) edge of GF-PMABS.



**Figure 12a.** AFM images of graphene oxide (a, b) and corresponding height profile (c)



**Figure 12b.** SEM images of graphene oxide on Cu grid (a, b) and Si foil (c, d)

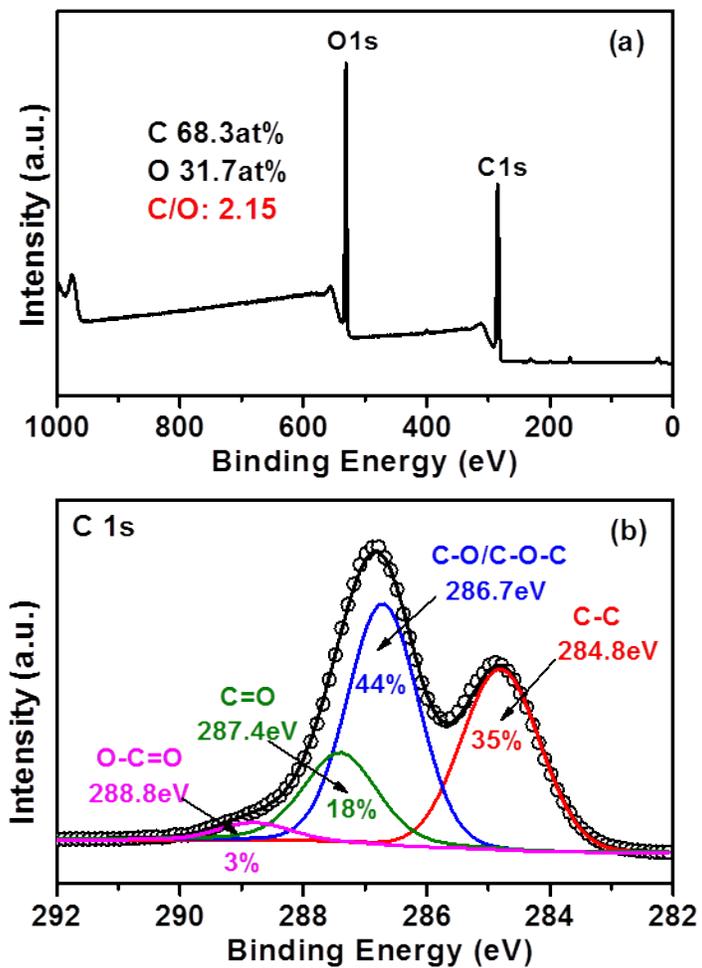


Figure 12c. XPS survey scan (a) and C1s (b) spectra of graphene oxide

## QCM measurements

Table S1. Frequency shifts in QCM measurements

	$\Delta f$ (Hz)		
	n=1 ( $\pm 1\%$ )	n=3 ( $\pm 2\%$ )	n=5 ( $\pm 3\%$ )
Uncoated crystal in electrolyte 25°C, $\Delta f_{b,25}$	-1550	-2370	-3100
Uncoated crystal in electrolyte 50°C, $\Delta f_{b,50}$	-1340	-1910	-2440
Polymer coated crystal in air 25°C, $\Delta f_p$	-3240	-9730	-16300
Polymer coated crystal in electrolyte 25°C, $\Delta f_{p,25}$	-4480	-11700	-18500
Polymer coated crystal in electrolyte 50°C, $\Delta f_{p,50}$	-4500	-11650	-18250
% weight change of polymer upon heating $\Delta M$	7	4	3

$$\Delta M = ((\Delta f_{p,50} - \Delta f_{p,25}) - (\Delta f_{b,50} - \Delta f_{b,25})) / (\Delta f_{p,25} - \Delta f_{b,25})$$

## References

1. Terayama, Y.; Kikuchi, M.; Kobayashi, M.; Takahara, A., *Macromolecules* **2010**, *44* (1), 104-111.
2. Sauerbrey, G. *Z. Phys. A.*, 1959, **155**, 206-222.
3. Martin, S.J. Granstaff, V.E. and Frye, G. *Anal. Chem.*, 1991, **63**, 2272-2281.
4. Johannsmann, D. *Phys. Chem. Chem. Phys.*, 2008, **10**, 4516-4534.