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Upper-critical solution temperature (UCST) polymer functionalized graphene oxide as thermally responsive ion permeable membrane for energy storage devices

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A thermally responsive membrane separator, suitable for use in non-aqueous electrolytes, was constructed by grafting a UCST polymer, poly(sulfobetaine), onto graphene oxide sheets. When heated from 20 to 80°C, it decreased the specific storage capacity of the electrode for Li by >50% reversibly, compared to 30% increase without polymer modification.

Stimuli-responsive and environmental-sensitive polymers and hydrogels[1-3] have been a subject of great interest due to their potential applications in, e.g. separation,[4] sensing,[5, 6] catalysis,[7] drug delivery,[8, 9] and biomaterials.[10] When incorporated into a membrane, they can provide gating functions to the transport of ions and molecules by reversibly changing the permeability and selectivity of the membrane, as well as altering the adsorptive or hydrophilic/hydrophobic properties.

Recently, there is an increasing interest to apply stimuli-responsive polymers to energy storage systems to mitigate the undesirable and potentially dangerous effect of thermal runaway. For example, Roberts and coworkers investigated an electrolyte composed of thermally responsive copolymer of acrylic acid and poly(N-isopropylacrylamide) (pNIPAM).[11] At low temperatures, pNIPAM is soluble, but phase segregates above the lower-critical solution temperature (LCST) and removes the ions from solution, thus causing a sharp decrease in the ionic conductivity of the electrolyte. In another example, Wei and coworkers used a coating of thermosensitive polymer P(N-isopropylacrylamide-co-2-acrylamido-2-methyl propane sulfonic acid) (P(NIPAM-co-SPMA)) to block access of ions to the pseudocapacitor material NiAl double layered hydroxide above LCST.[12] In these examples the polymers function in an aqueous system. Thus, they would not be suitable for higher voltage applications such as Li ion batteries or supercapacitors which use organic electrolytes. Thus far, no reversible thermal response systems have been reported for non-aqueous applications, and for them, methods to mitigate catastrophic thermal incidence include use of fire retardants or autonomous shut-down additives in the electrolyte,[13] positive temperature coefficient coatings on the electrode,[14, 15] and shut-down separators.[16] However,

once deplored, these processes are irreversible and the energy storage device is no longer functional.

We report here a thermal-responsive membrane that exhibits reversible changes in ion permeability in a non-aqueous electrolyte. Its main component is a grafted poly(sulfobetaine) polymer (PMABS) that has an upper-critical solution temperature (UCST) in an aqueous solution.[17-19] Our working hypothesis was that the UCST phenomenon also appears in polar organic electrolytes. The dipolar attraction between zwitterions in the polymer causes the polymer to coil tightly at low temperatures and form hydrophobic aggregates attached to the membrane, which permits unobstructed ion flux through open channels in the membrane. Above UCST the attractive interaction is disrupted and the polymer chains uncoil, exposing the zwitterions to the electrolyte. The potential consequences include change in the viscosity of the electrolyte inside the membrane due to polymer dissolution, and solvation of the zwitterions and their interaction with the electrolyte ions. Thus, the ion flux through the membrane would be hindered and the ionic permeability of the membrane would be lowered. Graphene oxide sheets were chosen to be the structural component of the membrane. It is electrically insulating, forms a self-supporting paper readily, and possesses oxygenate groups that can be used to graft poly(sulfobetaine).

Detailed preparation procedures can be found in Supporting Information. Briefly, graphene oxide (GO) was synthesized from flake graphite (Asbury Carbons, 230U Grade, High Carbon Natural Graphite 99+) using a modified Hummers method, by oxidation using solutions containing $K_2S_2O_8$ and P_2O_5 in concentrated H_2SO_4, $KMnO_4$ in H_2SO_4, and H_2O_2.[20] The final, bright yellow suspension was repeatedly centrifuged and washed with DDI water until the pH of the solution became neutral.

GO-PMABS was prepared by a surface-initiated atom transfer radical polymerization (SI-ATRP) process as shown in Figure 1.[21-23] In this process, an initiator was anchored onto the GO surface by first populating the GO with primary alcohol groups to form GO-OH. This was achieved by aminolysis of surface epoxide with 4-aminophenethyl alcohol in the presence of isopentyl nitrite and by reaction of the surface carboxylic acid groups with the aminoalcohol

to form diazonium salt. Esterification of GO-OH by reaction with α-bromoisobutyryl bromide to form GO-Br introduced the ATRP initiators. With this approach, a high loading of ATRP initiators could be introduced. SI-ATRP of MABS was accomplished with a $CuCl/CuCl_2$/bpy catalyst system, using a procedure modified from the literature (see SI for details).[24] The resulting suspension could be filtered, washed to remove soluble components, and dried to form a composite membrane GO-PMABS. In this method, no soluble polymer was formed, since the free radicals required for chain growth remained covalently anchored to the surface.
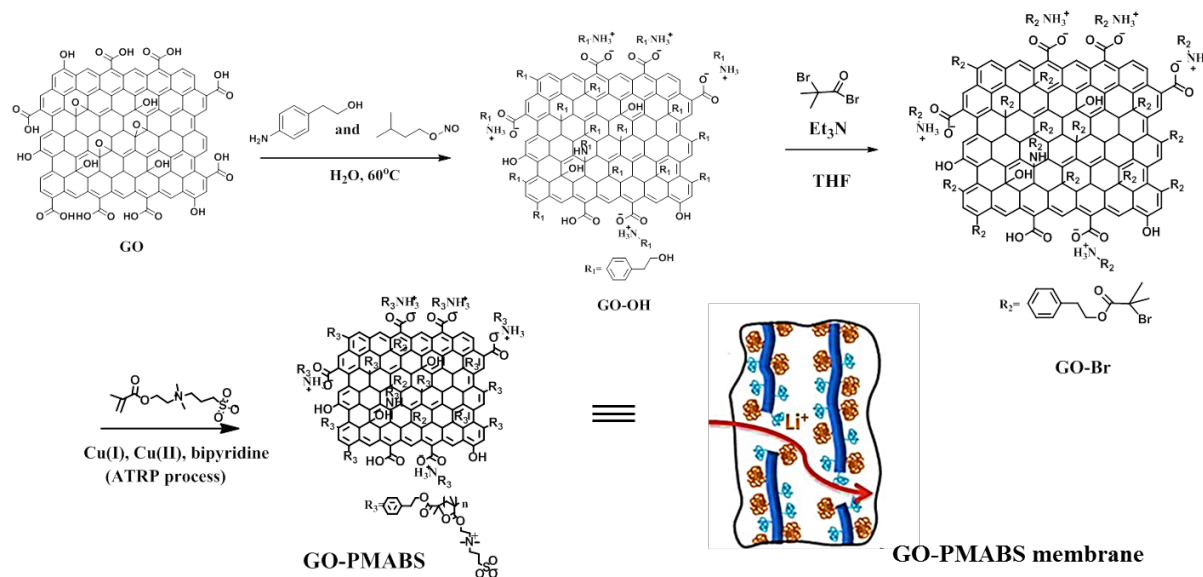

Figure 1. Synthesis of graphene oxide functionalized with poly(3-(N-2-methacryloyloxyethyl-N,N-dimethyl)ammonatobutane-sulfonate, GO-PMABS.
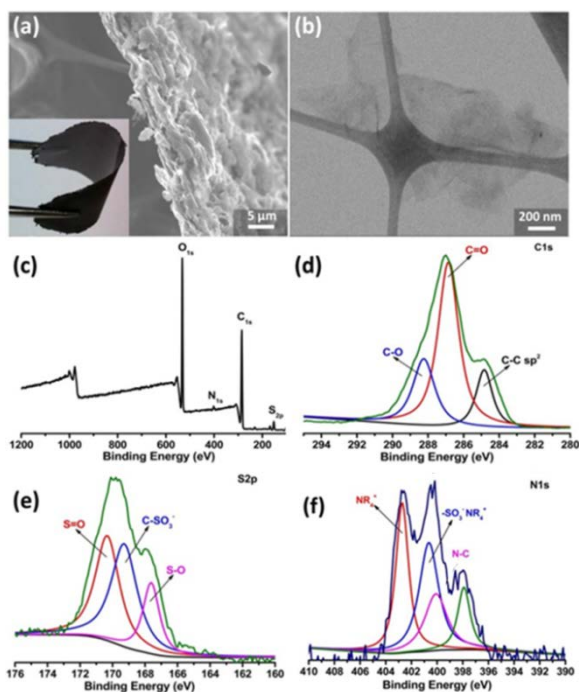

Figure 2. (a) Cross-sectional SEM image (inset digital image), and (b) TEM image of GO-PMABS. (c) XPS survey san, (d) XPC C1s, (e) S2p, and (f) N1s peak of GO-PMABS.

The self-supporting GO-PMABS membrane was relatively flexible (Fig. 2a inset). Its surface was more corrugated (Fig. 2a)

than that of GO (Fig. S5c), and a GO-PMABS membrane consisted of a stack of thin sheets. The roughened surface was consistent with the presence of polymer aggregates. TGA of GO-PMABS under a flow of N_2 showed ~70% mass loss over 300 - 500°C (Fig. S1) due to pyrolysis of the polymer, whereas a dried GO did not show mass loss in this temperature range. The fact that there was no weight loss below 100°C was consistent with the expected hydrophobic nature of GO-PMABS.

The shapes of the C_{1s}, S_{2p}, and N_{1s} XPS spectra of GO-PMABS (Fig. 2c-f) indicated the presence of multiple chemical species. The C_{1s} spectrum could be fitted to four peaks at 286.9 eV (C=O), 288.2 eV (C-O-C), and 284.8 eV (sp^2 C). The S_{2p} spectrum could be fitted to three peaks at 167.6, 169.3, and 170.3 eV, which could be two sets of overlapping doublets, one at 169.3 and 170.3 eV ($-SO_3^-$), and the other at 167.6 and 169.3 eV ($-SO_3^-$ NR_4^+).[25] The N_{1s} peaks could be fitted to three types of nitrogen: NR_4^+ (403.2 eV), $-SO_3^-$ NR_4^+ (400.6 eV, 400.1eV), and pyridinic N (398 eV). These spectra were consistent with the expected chemical composition of GO-PMABS.

The UCST behavior of PMABS could be observed visually. In water at 20°C, a 10 wt% PMABS (72 h) mixture was cloudy, but became clear at 50°C (Fig. S6). Although change in turbidity was not apparent in the organic carbonate solution, deposition of gel-like substance was observed on the flask wall when the solution was cooled from 80°C to room temperature, implying a decrease in solubility/miscibility.

The thermal response of Li ion permeability of the GO-PMABS membrane was tested by using it as a separator when measuring the Li ion-storage capacity of a reduced GO paper over the range 0.02-1.5 V when paired against a Li foil, at a constant current of 200 mA g^{-1} in a coin-cell battery assembly (see SI). The reduced GO paper

was prepared by reducing a graphene oxide paper at 850 °C in flowing Ar. The GO-PMABS membrane was sandwiched between two layers of glass fiber. A mixture of ethylmethyl carbonate and ethyl carbonate (7:3 v/v) containing 1.2 M $LiPF_6$ was used as the electrolyte. For measurements at elevated temperatures, the assembled coin cell was submerged in a silicon oil bath.

Figure 3. Specific charge storage capacity of reduced graphene oxide
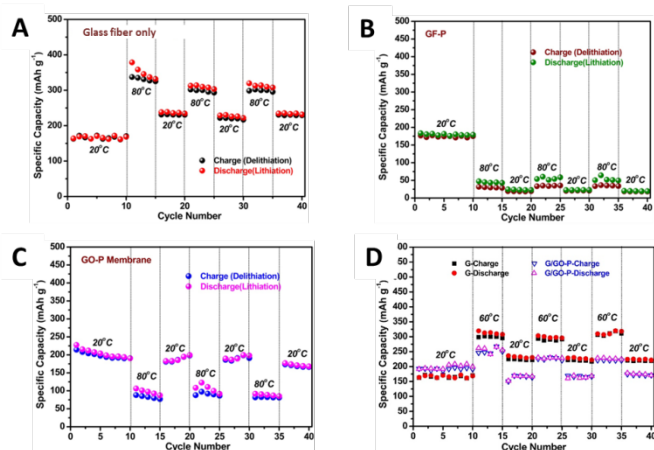
electrode, determined using a separator: (A) without GO-PMABS. (B) with GF-P. (C) and (D) with GO-PMABS. The voltage curves during charging and discharging are in Figure S7.

Two control experiments were also conducted. In one, the membrane separator was a layer of glass fiber. In another, the GO-PMABS in the sandwich membrane was replaced by GF-P. In the GF-P sample, the PMABS was only physically adsorbed and not grafted onto GF. In the first control experiment using only glass fiber as the separator, the charge storage capacity of the reduced graphene oxide was found to be ~170 mAh g^{-1} at room temperature, which increased to ~300 mAh g^{-1} at 80°C (Fig. 3A). The capacity dropped to ~ 220 mAh g^{-1} when the cell was returned to room temperature. This behavior was repeatable over many cycles, and was likely due to reduced viscosity of the electrolyte at the higher temperatures, and thus higher ion mobility and ion flux, and higher storage capacity over the same voltage window. In contrast, when GO-PMABS was in the separator, the storage capacity decreased from ~200 mAh g^{-1} at room temperature to ~100 mAh g^{-1} at 80°C. Again, this change in capacity with temperature was repeatable over many cycles. Thus, in the presence of grafted GO-PMABS, the ion permeability of the separator decreased at elevated temperatures. It is interesting to note that retarding of ion permeability was apparent only >60°C. There was no obvious effect of PMABS modification up to 60°C (Fig. 3). It should be mentioned that another natural control experiment of using unmodified GO instead of GO-PMABS led to highly unstable current-voltage behavior at elevated temperatures due to chemical reaction of Li salt electrolyte with the oxygenated functional groups on GO.

It is important that PMABS was covalently linked to GO. In the second control experiment, GF-P, in which the polymer was introduced by impregnation, was used in the separator. In the first heating cycle, the storage capacity decreased from ~170 mAh g^{-1} at room temperature to ~40 mAh g^{-1} at 80°C. But the capacity could not be restored when the system returned to room temperature. In fact, the storage capacity was lost irreversibly after one heating cycle. This can be explained by the fact that at 80°C, the PMABS

dissolved in the electrolyte and diffused away from the separator membrane. Upon subsequent cooling, the polymer segregated out from the electrolyte and was deposited everywhere, including the electrodes. This blocked the electrode and negatively impacted its charge storage capacity.

The system was further characterized with other techniques, including quartz crystal microbalance (QCM), cell impedance, and UV-vis spectroscopy of electrolyte solution. In the QCM measurement, the frequency shifts of a layer of PMABS, spin-coated onto a quartz crystal, were recorded after the sample was submerged in an electrolyte (Li salt in organic carbonate) solution at 25 and 50°C (upper temperature limited by instrument capability). Baseline frequency shifts due to liquid loading and the thermal effects of the solvent (e.g. viscosity changes) and other instrument effects were first determined using data from an uncoated crystal collected under identical conditions and a coated crystal in air. Any remaining frequency change attributable to thermal effect of the PMABS layer was within experimental uncertainties (Table S1). This implied the presence of the polymer layer did not cause detectable changes in the apparent weight and/or viscosity near the crystal surface up to 50°C, consistent with the hypothesis PMBAS was immiscible with the carbonate solution at that temperature and the observation on the charge storage capacity.

The cell impedance with or without GO-PMABS were collected at OCV, and the data are shown in Fig. S8. At room temperature, the Nyquist plots were similar with or without GO-PMABS in the separator, roughly equal charge transfer/polarization resistance based on the high frequency data (R_{ct}, 118 Ω without and 97 Ω with GO-PMABS). This suggested that the properties of the electrolyte and electrodes were not affected by the presence of GO-PMABS. Upon heating to 60°C, the charge transfer/polarization resistance was lowered to ~12 Ω for the sample without GO-PMABS, and to ~34 Ω with GO-PMABS. This decrease in resistance was consistent with the lower viscosity of the electrolyte and the corresponding increase in ionic conductivity at higher temperatures.[26, 27] There was not much difference between 60 and 80°C.

The cyclic voltammetry curves of the reduced graphene oxide electrode were similar whether the separator contained GO-PMABS or not (Fig. S9). Thus, there was no detectable electrochemical reaction associated with the presence of GO-PMABS.

We also attempted to use UV-vis spectroscopy to probe binding of Li ions to the polymer. The UV spectrum of $LiNO_3$ in EC/DMC showed an intense absorption peak at ~225 nm due to absorption by the nitrate ion. The intensity of this peak, collected with the clear portion of the solution, decreased after adding GO-PMABS into the solution, suggesting binding of nitrate, and by inference Li ions, onto the polymer. The peak intensity decreased further slightly at 60 °C (Fig. S10).

Conclusions

We have shown that a membrane, modified with a UCST polymer, can function to restrict ion flow reversibly at elevated temperatures. This was demonstrated using a PMABS-modified graphene oxide, and applied it to an assembly that resembles a Li ion battery. Since the upper critical solution temperature depends on the nature of the polymer and the solvent, such as molecular weight and density and nature of the zwitterions, there are many revenues available to tune the transition temperature and magnitude of change of ionic permeability. For example, we expect that the transition temperature would be higher for a larger molecular weight polymer with a higher density of zwitterions. Because the thermal effect is reversible, this type of membranes can find applications not only in energy storage, but also in sensors and purification and electrochemical systems. For energy storage, such a membrane could

be useful in mitigating thermal runaway in batteries by suppressing ion mobility at elevated temperature, thereby reducing the charge/discharge rates and heat generation. It can also provide the function of internal cell-balancing by restricting local ion flow in regions where the charge transfer is too rapid and heat generation is too fast due to inhomogeneity of the electrodes. The successful demonstration of the concept suggests further development is warranted for these applications.

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Notes and references

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Electronic Supplementary Information (ESI) available: Materials, synthesis details, and characterization methods; results from TGA, XPS, SEM, EDAX, TEM of GO, GO-Br, GO-PMABS; UV spectra of GO-PMABS with $LiNO_3$ in organic carbonate; QCM results; CV curves; Nyquist of GO-PMABS. See DOI: 10.1039/b000000x/

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