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Graphene Oxide Annealing Procedures for Graphene-Based Supercapacitors

by Louis B Levine and Matthew H Ervin

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Graphene Oxide Annealing Procedures for Graphene-Based Supercapacitors

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14. ABSTRACT Graphene is an excellent material for energy storage devices such as supercapacitors. Graphene can be deposited onto a substrate for device construction in multiple ways. One method is to deposit graphene oxide (GO) onto a surface and reduce it, resulting in reduced graphene oxide (rGO). There are many methods of reduction possible; this report discusses thermal reduction. Our goal is to outline a procedure for the thermal reduction of GO to optimize the performance of supercapacitors. We also demonstrate thermally assisted ionic liquid electrolyte wetting of the electrodes, as well as our initial attempts at making high operating temperature supercapacitors.					
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1. Introduction and Background

Graphene has become very popular for electronic devices in the last few years as a material with outstanding electrical and mechanical properties. Graphene's high surface area, excellent electrical conductivity, and electrochemical inertness make it an attractive electrode material for use in supercapacitors. Graphene can be produced through the chemical oxidation and exfoliation of graphite to produce single-layer (SL) graphene oxide (GO). GO can then be reduced through multiple methods, such as thermal reduction, to produce conductive graphene (reduced GO [rGO]) (Zhu et al. 2010). The driving force behind such a thermal reduction is the loss of oxygen-containing functional groups (e.g., COOH) from the GO, which has been reported in the literature to occur at 180 °C and above (Huh 2011). Additional losses may occur at temperatures above 600 °C, but these changes do not seem to be useful for supercapacitor applications because they also encourage restacking of the graphene into graphite (reducing surface area and therefore capacitance).

This report details our findings for using thermally reduced GO to create graphene-based supercapacitors with aqueous and ionic liquid (IL) electrolytes. ILs are electrolytes that enable higher voltage and higher temperature performance. We have found that some ILs do not wet well when using electrodes that have already been annealed, which prompted us to create new reduction and electrolyte wetting procedures.

Here we determine the minimum requirements for the optimal thermal reduction and IL wetting of these electrodes. Procedures for reducing and wetting graphene electrodes with ILs will be useful for making high service temperature devices, where aqueous electrolytes cannot be used. Such high service temperature devices will enable a wide range of applications in munitions and engine compartments, as well as increased shelf life. Toward this end, we have performed some initial studies on high temperature device fabrication.

2. Experiment and Calculations

There are 3 different methods of anneal described in this report: dry anneal, dry/wet anneal, and wet anneal. All 3 procedures are similar to each other. In all the procedures, common materials were used. GO was purchased from www.cheaptubes.com (dispersed SLGO 99% in deionized [DI] water, 2 mg/ml). The IL electrolytes used were 1 butyl-3-methyl-imidazolium tetrafluoroborate ([BMIM][BF₄]) 98%, purchased from Strem Chemicals, and 1-ethyl-3-methylimidazolium dicyanamide (EMI-DCA) from Sigma-Aldrich. A 0.5M

potassium sulfate (K_2SO_4) solution, also from Sigma-Aldrich, was used for the aqueous electrolyte.

2.1 Device Fabrication

The devices were made as either coin cells or flexible pouch cells.

All coin cells were packaged in stainless steel CR2032 housings, with Celgard 3501 as the polymer separator. To make the electrodes, stainless steel current collectors are set on a 90 °C hot plate to promote drying, and the GO dispersion is applied in 25- μl volumes with a micropipette. Six applications of the GO solution are uniformly deposited over approximately a 1.8- cm^2 surface area, waiting in between layers for it to dry. After an anneal procedure (below) to reduce the GO to rGO, electrolyte (if a dry anneal) and a separator is added, and the cell is sealed.

Pouch cells were used for elevated temperature testing as the coin cell polymer seals fail at 70 °C. For pouch cells, the current collectors are 2 x 2 cm plus a long lead, stainless steel foils. Again, current collectors are placed on a hot plate to promote drying, and dispersed GO is applied in six 50- μl quantities, waiting in between each deposition for the GO to dry. After annealing, electrolyte (if a dry anneal) and a high temperature Dreamweaver Gold 40 separator material obtained from Dreamweaver International are used. These electrodes, separator, and IL are placed in a pouch made of fluorinated ethylene propylene (FEP)-coated Kapton, which is heat sealed on all 4 sides. The Kapton with FEP coating was obtained from American Durafilm.

2.2 Dry Anneal

A dry anneal refers to annealing the GO drop cast electrode in an oven without any electrolyte. This procedure was only used for aqueous electrolytes, because in our experience, [BMIM][BF₄] did not wet properly without additional treatment. To determine the proper anneal temperature, electrodes were annealed at temperatures ranging from 140–240 °C at 20 °C increments. A follow-up experiment involved annealing different samples at 180 °C for varying amounts of time, ranging from 30 min to 16 h. After annealing, the electrodes are packaged with 20 μl of K_2SO_4 per electrode (total 40 μl per cell) and the separator before sealing the cell.

When this dry anneal was used in conjunction with IL electrolytes, poor device performance resulted. Since we suspected that this poor performance may be due to poor IL electrolyte electrode wetting, we devised new electrode anneal procedures to address this. These procedures is referred to as dry/wet anneal, wet anneal, and solvent-assisted wetting.

2.3 Dry/Wet Anneal

A dry/wet anneal is identical to the dry anneal procedure, except for the addition of 2 extra steps. The electrodes were first reduced at 180 °C for 4 h. After this thermal reduction, 10 µl of [BMIM][BF₄] was added to each electrode. These electrodes with IL were then heated in an oven at various temperatures to diffuse the ILs into the electrodes. The temperatures used were between 100 and 220 °C at 40 °C intervals. Afterwards, the cells were heated at 110 °C in a vacuum oven to drive off any water, before being packaged and sealed in a dry room.

2.4 Wet Anneal

The last method of anneal to be described in this report is a wet anneal. Here, each drop cast electrode is covered with 10 µl of IL. These electrodes were then annealed for 4 h at temperatures ranging from 180 to 280 °C, at 20 °C intervals. In some cases, at high temperatures where there was significant IL loss or apparent degradation, more IL was added as the cell was being packaged. Again, the electrodes were heated at 110 °C in a vacuum oven to drive off any water, before being packaged and sealed in a dry room.

2.4.1 Solvent Assisted Wetting

Non-thermally enhanced IL wetting of the electrodes was attempted by thinning the IL with solvents such as alcohol or dimethylformamide (DMF) and then testing the electrodes with the solvent left in place or evaporated prior to testing.

2.5 Electrochemical Testing

All data were collected on a Princeton Applied Research 4-channel VersaStat MC potentiometer, with the provided software. Cyclic voltammetry (CV) testing parameters varied, but in general, devices were tested at scan rates of either 20 or 100 mV/s, with voltage ranges of 0–1 V for the aqueous electrolyte and 0–2.5 V for the IL electrolytes. Electrochemical impedance spectroscopy (EIS) was carried out from 100 kHz to 5 MHz at 0 V. Before running an EIS scan, devices were stabilized at 0 V for 10 min to ensure that the devices were fully discharged. To create a Ragone plot, charge rates between 0.025 and 25 A/g were used, charging the device to 2.5 V before discharging. This was done twice per charge rate to ensure accuracy, and energy and power densities were calculated using the second discharge cycle.

2.6 Calculations

Capacitance in this report was measured using CV or EIS methods:

- CV method: The difference between the currents measured at the middle of the CV range during the forward and reverse scan directions is divided by 2 to obtain a representative (dis)charging current for the device. This current is divided by the scan rate to get the capacitance of the cell.
- EIS method: Using the graph of capacitance (C_{re}) versus frequency, the peak capacitance value within our frequency range, which is typically found at or near the lowest frequency measured (1 MHz), was used.

In order to determine the mass normalized values for capacitance, the total mass of the rGO cell was used. The blank current collectors were weighed before and after drop casting of the GO, and again after the thermal reduction. The rGO mass in the cell (for dry anneal and dry/wet anneal only) is calculated by subtracting the current collector masses from the annealed electrode masses. The measured cell capacitance is divided by the total rGO mass in the cell and the result is multiplied by 4 to obtain the specific capacitance, in terms of F/g, using the single electrode convention for reporting specific capacitance.

For the wet anneal procedure, the mass of the electrodes after anneal cannot be obtained due to the unknown mass of the IL, so a mass equal to $45\% \times$ the mass of the deposited GO was used. This estimate is based on the mass loss seen with a dry reduction of the GO.

3. Results and Discussion

One method of determining the effectiveness of the GO anneal is to assess how much mass is lost during reduction. Table 1 reports the electrode masses as-deposited and after thermal annealing at various temperatures. In general, mass losses of 40% were indicative of full thermal reduction of the GO, as determined by the performance of the devices. Literature values of mass loss during reduction are around 30%, our higher values may include the loss of water left in the electrodes after drop casting (Dreyer et al. 2010, p 236). Mass losses considerably higher than 30–40% in Table 1 may be due to flaking of the rGO during the anneal. This is common at higher temperature anneals, and is likely caused by the expansion and contraction of the rGO on the current collector during heating and cooling, as well as drying.

Table 1 Gravimetric analysis of the reduction of GO to rGO

Anneal Temp (°C)	Sample	Mass (mg)		
		Drop Cast GO	Post Anneal rGO	Percent Mass Lost During Reduction (%)
140	A	0.328	0.262	20.1
	B	0.312	0.250	19.9
160	A	0.320	0.230	28.1
	B	0.324	0.238	26.5
180	A	0.320	0.182	43.1
	B	0.320	0.184	42.5
200	A	0.314	0.160	49.0
	B	0.314	0.162	48.4
220	A	0.306	0.150	51.0
	B	0.326	0.166	49.1
240	A	0.317	0.154	51.4
	B	0.318	0.158	50.3

3.1 Dry Anneal

The first anneal experiments were done using the dry anneal process and K_2SO_4 electrolyte. The resulting electrode capacitance was measured as a function of anneal temperature over a range of 140–240 °C for 4 h. As seen in Fig. 1, the capacitance of the devices was poor until an anneal temperature of around 180 °C, and raising the temperature after this point did not have a great effect. For samples that were considered fully reduced in this figure (180 °C and above), the capacitance increased when cycling before stabilizing, while partially reduced samples (140 and 160 °C) decreased in capacitance before stabilizing. This indicates there is a greater life cycle for samples that are fully annealed. Comparisons of the CV tests in Fig. 2 between 160 and 200 °C anneals shows an increasing capacitance with increasing anneal temperature up to 180 °C. This is in agreement with literature (Huh 2011) values showing maximum obtainable reduction without graphene restacking at 180 °C. Generally, the reduction at 180 °C was very good, and close to what we assume is full reduction at 240 °C. It should be noted that while 180 °C is acceptable as a temperature for these dry anneals, an anneal temperature of 200 °C produces more consistent results. In general, we have found that samples annealed at 180 °C may have slightly worse performance or lower mass lost during annealing than the 200 °C or higher anneals. In Table 1, the 180 °C anneal shows a lower mass loss than the 200 °C anneal, yet displays similar performance (Fig. 1).

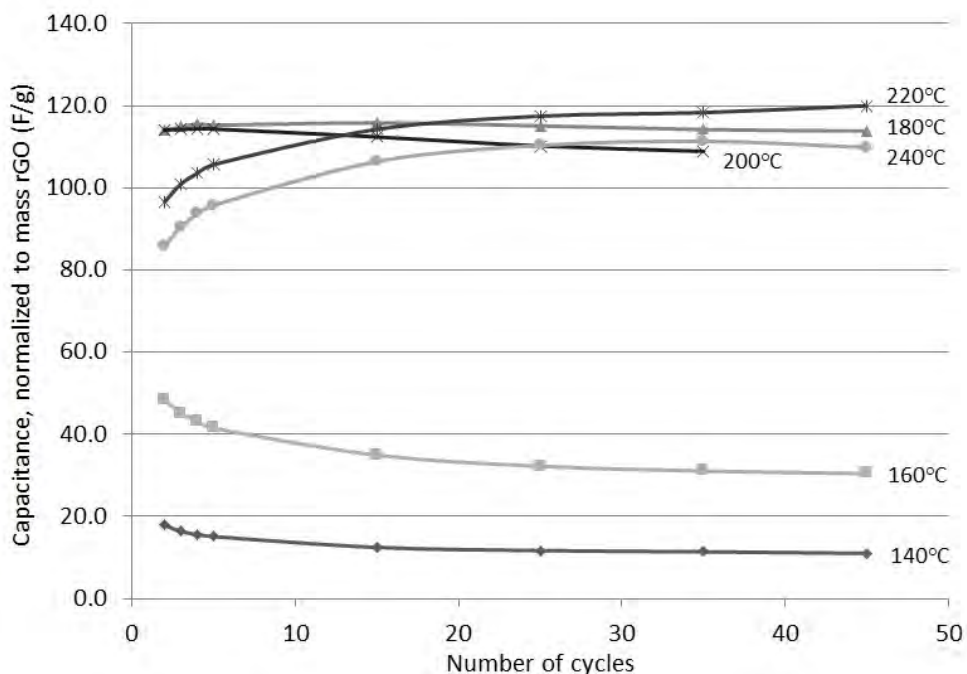


Fig. 1 Specific capacitance as a function of CV cycling for electrodes dry annealed at various temperatures and tested at 20 mV/s from 0.0 to 1.0 V with K_2SO_4 electrolyte

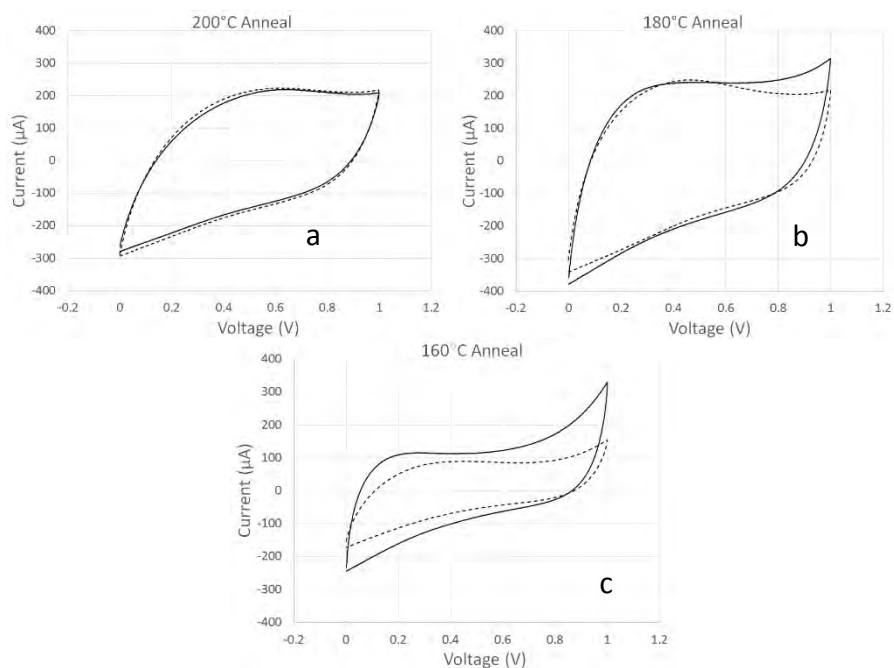


Fig. 2 CV plots taken with K_2SO_4 electrolyte for electrodes annealed for 4 h at a) 160 °C, b) 180 °C, and c) 200 °C. The 5th (solid) and 45th (dashed) CV cycles are shown to give an idea of how stable the capacitance is with cycling. The large increase in capacitance between a) and b) is believed to be due to the more complete reduction of the GO at ~180 °C (Huh 2011, p 77). No significant improvement was observed after b).

Once a minimum reduction temperature was established for an anneal time of 4 h, the anneal time was optimized. GO samples were created and then annealed at 180 °C for different lengths of time, from 30 min up to 16 h. Figure 3 compares the capacitance with repeated cycling for these different anneal times.

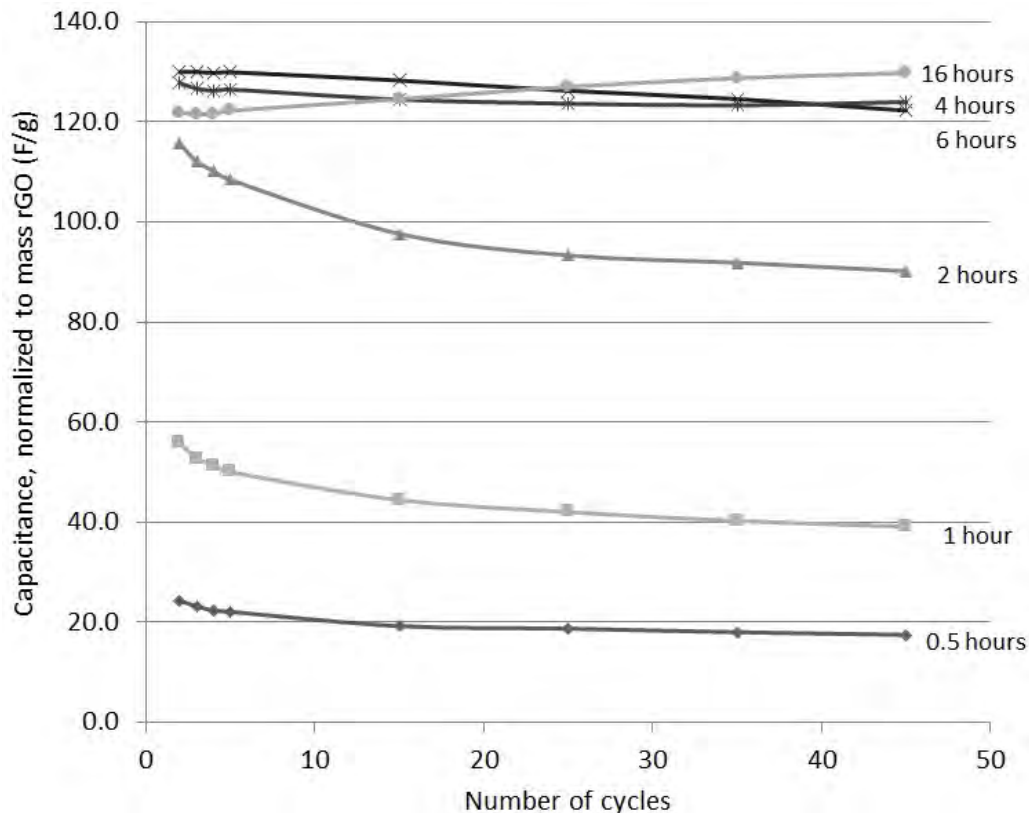


Fig. 3 Specific capacitance as a function of CV cycling for electrodes dry annealed at 180 °C for various anneal times, showing that anneal times of 4 h or greater produced the best devices. These devices were tested at 20 mV/s from 0.0 to 1.0 V with K₂SO₄ electrolyte.

It appears that any amount of time less than 4 h is insufficient at this temperature. While 2 h may initially appear acceptable, the capacitance decreased significantly during the initial cell cycling. The 4-, 6-, and 16-h anneals resulted in higher and more stable capacitances. Increasing the time of anneal beyond the required 4 h (such as for an overnight anneal, 16 h) is not destructive to the graphene, but provided no significant additional benefit.

We determined that 4 h at 200 °C should be the minimum time used for reliable dry anneals; however, the required time of anneal will be affected by the temperature. For example, in an extension of this dry anneal optimization experiment, high temperature anneals of 400–800 °C were carried out for only 1 h. While capacitance values were not particularly good for these samples, gravimetric analysis of the rGO on the current collectors after anneal indicates that the GO was sufficiently

reduced in a shorter period of time. There was some delamination and flaking of the rGO on these electrodes, which probably contributed to the poor performance, but the mass lost during anneal was comparable to the values in Table 1. It is also possible that restacking of the graphene is occurring at these higher temperatures (Huh 2011), which would reduce surface area and therefore capacitance. Conversely, for devices that may require low temperature processing due to packaging limitations, the length of the anneal time could be increased while decreasing the temperature, although full reduction of the GO may not take place below 180 °C.

3.2 Dry/Wet Anneal

We found that some ILs produced low capacitance devices when using the dry anneal approach. We suspect that this is due to poor wetting of the electrode by the electrolyte. In order to promote better wetting, the IL was heated to reduce its viscosity and allow it to permeate the graphene pore networks. This was done by 1 of 2 procedures:

- 1) Dry/wet anneal: IL is put on after a dry electrode anneal and reheated, or
- 2) Wet anneal: IL is applied before the electrode annealed.

Both of these processes were investigated to determine whether improved capacitances could be achieved while using IL electrolytes.

The dry/wet anneal samples were baked at 180 °C for 4 h dry to fully reduce the GO, before [BMIM][BF₄] IL was applied and the samples were heated again wet. Initially, it was uncertain if the IL would wet with only mild heating, so a range of temperatures were investigated for the IL anneal. In Fig. 4, large jumps in capacitance can be seen when the anneal temperature is increased from 140 to 180 °C, as well as from 180 to 220 °C. However, under the conditions tested, this dry/wet anneal procedure produces lower mass normalized capacitance values (on the order of 10 F/g or less) when compared to the wet anneal approach described in Section 3.3.

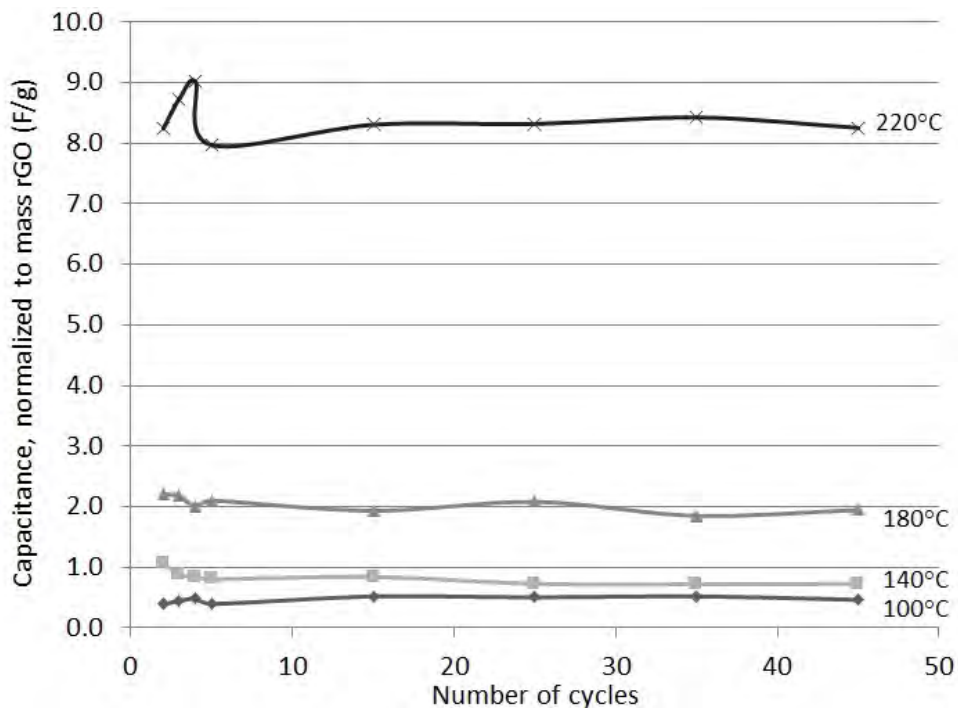


Fig. 4 Capacitance as a function of CV cycling for electrodes dry annealed and then wetted with IL at the temperatures, showing that dry/wet annealed devices had a significant performance increase when heated with the IL at temperatures above 180 °C. These devices were tested at 20 mV/s from 0.0 to 3.0 V using [BMIM][BF₄] electrolyte.

3.3 Wet Anneal

One of the goals with the wet anneal process is to cut down on processing time by annealing the GO and heating the IL at the same time, thus 4 h of processing is eliminated. But it is also expected that by annealing the GO with the IL on the electrodes, the liquid will permeate the graphene network better than with the dry/wet anneal process. This is because the oxygen functional groups, which are still on the GO sheets at the beginning of the anneal, should make the electrode more hydrophilic, which may assist the permeation of the IL throughout the electrode (Zhu et al. 2010). This, in turn, should raise the capacitance of the device by increasing the accessible surface area of the electrode. While this mechanism is still speculation, we did see superior performance from wet anneal devices (Fig. 5). A wet anneal temperature of 220 °C for 4 h resulted in optimal performance in terms of F/g. In addition, at higher wet anneal temperatures, shorter anneal times can be used with little reduction in performance. For instance, devices annealed at 240 °C for only 30 min are found to be sufficiently annealed. We use this anneal in subsequent experiments. We see in Fig. 5 that with wet anneal temperatures above 240 °C for 4 h, the device performance starts to decrease, possibly due to the degradation of the IL. It is interesting to note that the 180 °C wet anneal is

insufficient. It is not clear if there is insufficient wetting at this temperature or whether the presence of the IL stabilizes the oxygen containing functional groups so that they don't reduce until higher temperatures.

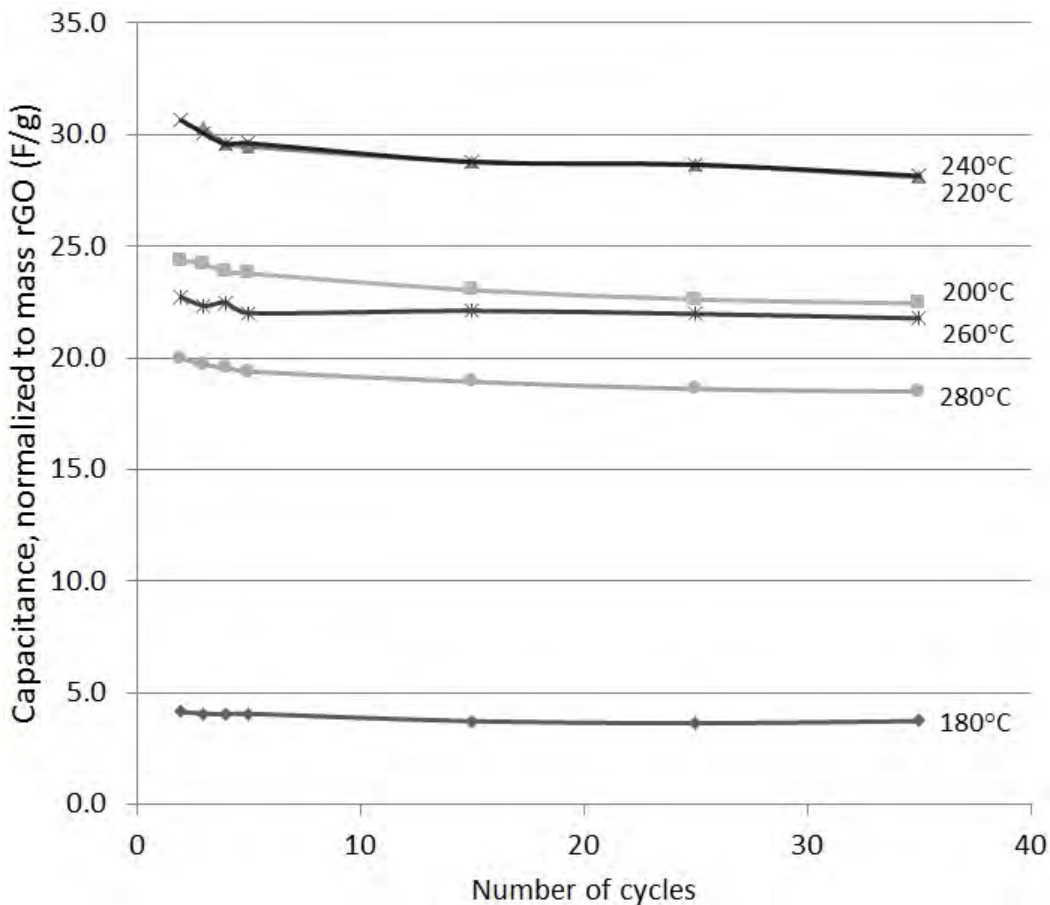


Fig. 5 Capacitance as a function of CV cycling for GO electrodes simultaneously reduced and wetted with IL at various temperatures, showing that temperatures below 220 °C are not sufficient for wet anneal and performance decreased with anneal temperatures above 240 °C, possibly due to IL degradation. All anneals were for 4 h, and the devices were tested at 20 mV/s from 0.0 to 3.0 V with [BMIM][BF₄] electrolyte.

We believe the dry/wet and wet anneal methods work through a reduction of the IL's viscosity, allowing it to more easily permeate the pore network of the graphene and have access to higher surface area of the device. In an effort to verify that the wet anneals increase the capacitances by reducing the IL viscosity and study the effects of IL viscosity on device performance, a set of experiments was carried out where a lower viscosity solvent was mixed with the IL. In this way, the viscosity of the IL is decreased chemically instead of thermally. Ethanol, isopropanol, and DMF were tested, with DMF producing the best results. Using DMF-thinned IL, electrodes could be wetted at lower temperatures after an initial dry anneal.

Using a 1:1 ratio of DMF to [BMIM][BF₄], 2 cells were made: in the first cell, the DMF was removed from the cell by heating it briefly to 180 °C; in the second cell, the DMF was left in the cell. Both cells produced acceptable capacitance values of 10–20 F/g, which are significantly greater than can be achieved with room temperature (RT) IL wetting without solvent. Consistent for both of the cells processed with DMF was good life-cycle endurance. After over 1,000 cycles, the cells still had a significant amount of capacitance left (Fig. 6). While the cell with DMF left in showed worse performance, our sample size is not significant enough to make a conclusion about the effect of DMF in the cell.

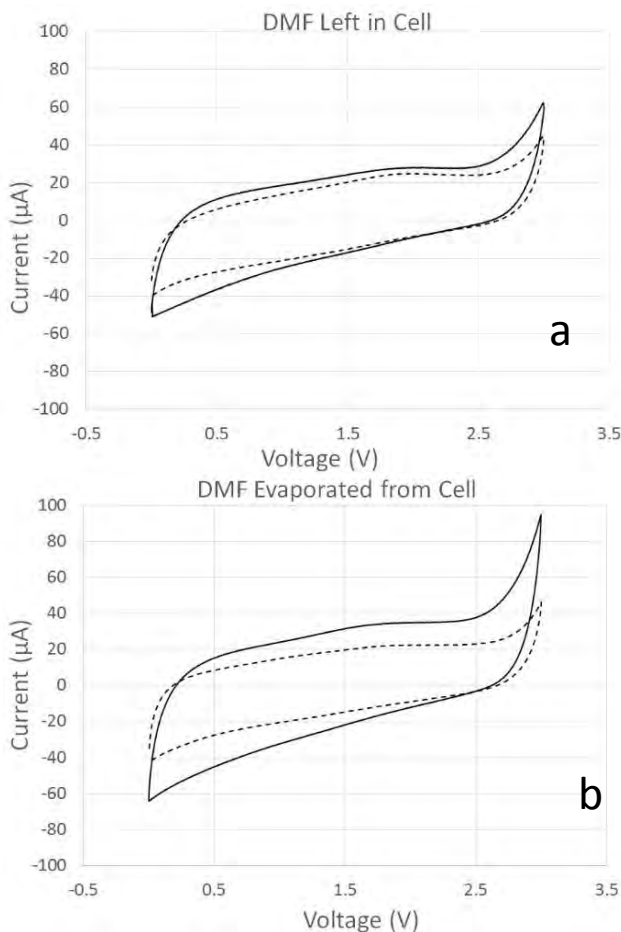


Fig. 6 Life-cycle testing of DMF-thinned IL cells: a) DMF evaporated out of cell: 66% of peak capacitance after 1000 cycles and b) DMF left in the cell: 91% of peak capacitance after 1000 cycles. Initial capacitance is the solid line, capacitance after 1000 cycles is the dashed line. These devices were tested at 0–3.0 V, 20 mV/s.

With the understanding that lowering the viscosity of the IL increases the wetting of the electrodes, new devices were created to see if increasing the ratio of solvent to IL would further improve performance (Qiao et al. 2011). Four cells, with ratios of 0:1, 1:1, 2:1, and 3:1 DMF:IL by volume were compared (Fig. 7). As the ratio

of DMF:IL is increased, we see an almost linear increase in capacitance. The results of these experiments show that the reduction of viscosity, whether by adding a solvent or heating the IL with a wet anneal, is a plausible explanation for the increase in performance when using ILs. While it is also possible that the solvent increases performance by increasing the IL conductivity due to an increase in ion mobility resulting from decreased electrolyte viscosity, EIS measurements do not show a clear trend of increased electrolyte conductivity. Increased wetting by reducing IL viscosity is an explanation that is also supported by the dry/wet anneal procedure, where an increase in performance is retained at RT (unchanged conductivity) after the IL anneal (increased wetting).

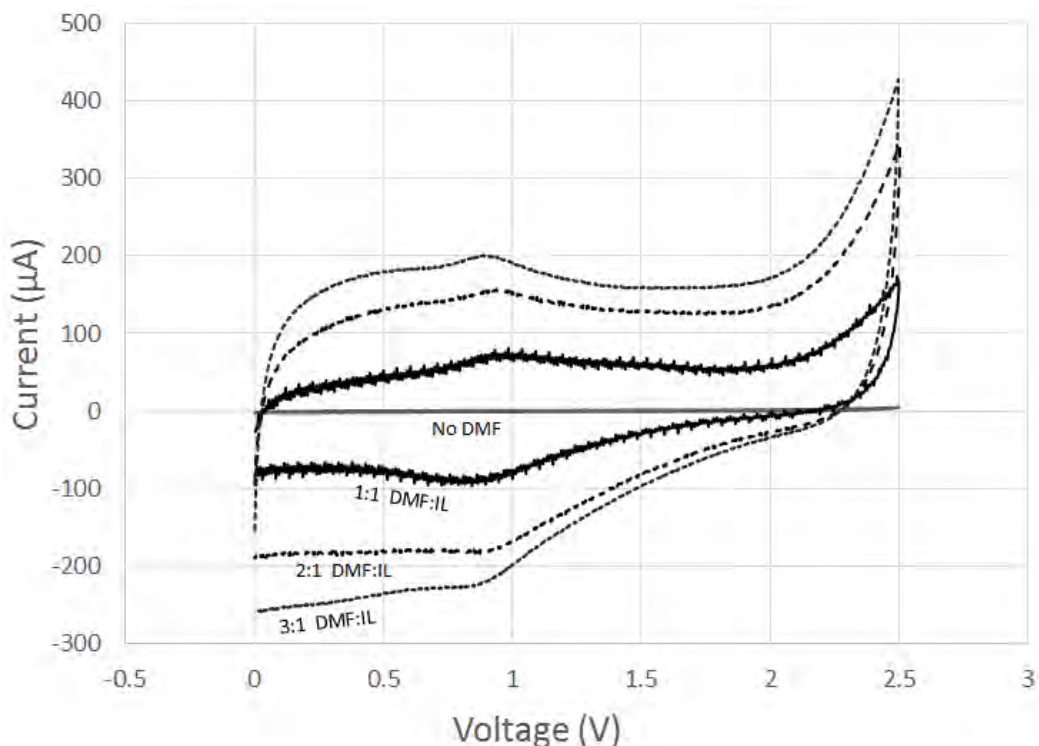


Fig. 7 CV plots of devices made with varying amounts of DMF in the IL: no DMF, 1:1 DMF:[BMIM][BF₄], 2:1, and 3:1 ratio, showing device performance improved significantly with increasing DMF concentration, presumably due to decreasing viscosity. Capacitance for these devices were 0.77, 36.7, 77.5, and 92.3 F/g, respectively. These CV scans were performed at 20 mV/s.

One problem encountered with the DMF-thinned cells is that they often required a long burn in time. Some devices required hundreds of CV cycles for the capacitance to stabilize, others only a few dozen (the measurements shown in Fig. 7 grew quickly and stabilized after 15–25 cycles). This burn in growth can be as large as 800% before the capacitance settles. This means that more processing may be required to obtain a stabilized device. The cause for this initial growth period is unknown, but it may be the result of electro-wetting of the electrodes.

4. Application: High Operating Temperature Flexible Device

The main goal of these anneal experiments above was to create procedures for reducing GO and make better devices with IL electrolytes. IL electrolytes are interesting for making higher voltage devices, as well as devices with operating temperatures over 100 °C where aqueous electrolytes and traditional organic electrolytes are not usable. However, in order to make a high operating temperature device, there are a number of components that must be able to withstand the temperature in addition to the electrolyte.

The coin cells used for the experiments earlier in this report use plastic seals that melt at around 70 °C. Therefore, flexible high temperature compatible Kapton pouch cells were used (Ervin et al. 2014). Another thermal constraint in our cells is the polymer separator: the Celgard separators used in the coin cells melt at temperatures less than 150 °C. An alternative aramid separator was used, Dreamweaver Gold 40 μm (Dreamweaver Intl), which is designed for high temperature applications. Also, binders commonly used in graphene supercapacitors (polyvinylidene fluoride, styrene butadiene rubber, etc.) to promote electrode material cohesion and adhesion to the current collector, will not withstand elevated temperatures, so binder-free electrodes were used for these experiments.

The most successful anneal procedure for our rGO/IL devices was a wet anneal at 240 °C for 30 min. Using a shorter anneal time proved to be useful in preventing a loss of adhesion of the graphene to the current collector. With longer anneal times, the IL would get under the graphene and cause it to flake from the current collector.

Many types of current collector materials were tested: nickel (Ni), stainless steel, and titanium (Ti) foils, and evaporated metals on Kapton (Ti/platinum [Pt], chromium [Cr]/Pt, and Pt). The Ti foil samples did not perform past temperatures of 150 °C, possibly due to a reaction between the titanium and the IL. The Ti/Pt, Cr/Pt, and Pt on Kapton samples had acceptable performance, but we encountered problems with metal separating from the Kapton during processing and cycling at temperature. Some reasonable success was achieved with these devices if the evaporated metal samples were annealed quickly before drop casting the GO. Ni foils were also acceptable, but had worse cycle life than stainless steel type foils; it is possible that the interface between the Ni and graphene worsens over time. The best current collector material we found was stainless steel foil, as there are no issues with flaking during anneal as with the metal/Kapton current collectors, nor a chemical reaction between the IL and the metal.

Samples made with stainless steel foil and [BMIM][BF₄] IL performed well, and had good capacitance when pushed to the thermal limits of the cell (68 F/g at

250 °C, when the IL begins to show visible discoloration and capacitance degradation [Fig. 8]). Capacitance values increased when the devices were heated, in 1 device, to about 150% of the RT capacitance at 150 °C (Fig. 8). From there, capacitances were relatively stable until the temperature was increased to 250 °C. The decrease in capacitance at 250 °C appears to be due to IL or perhaps separator degradation, but it could also be due to the “normal” cycle life degradation of the device seen at RT, since the same device was repeatedly cycled at successively higher temperatures.

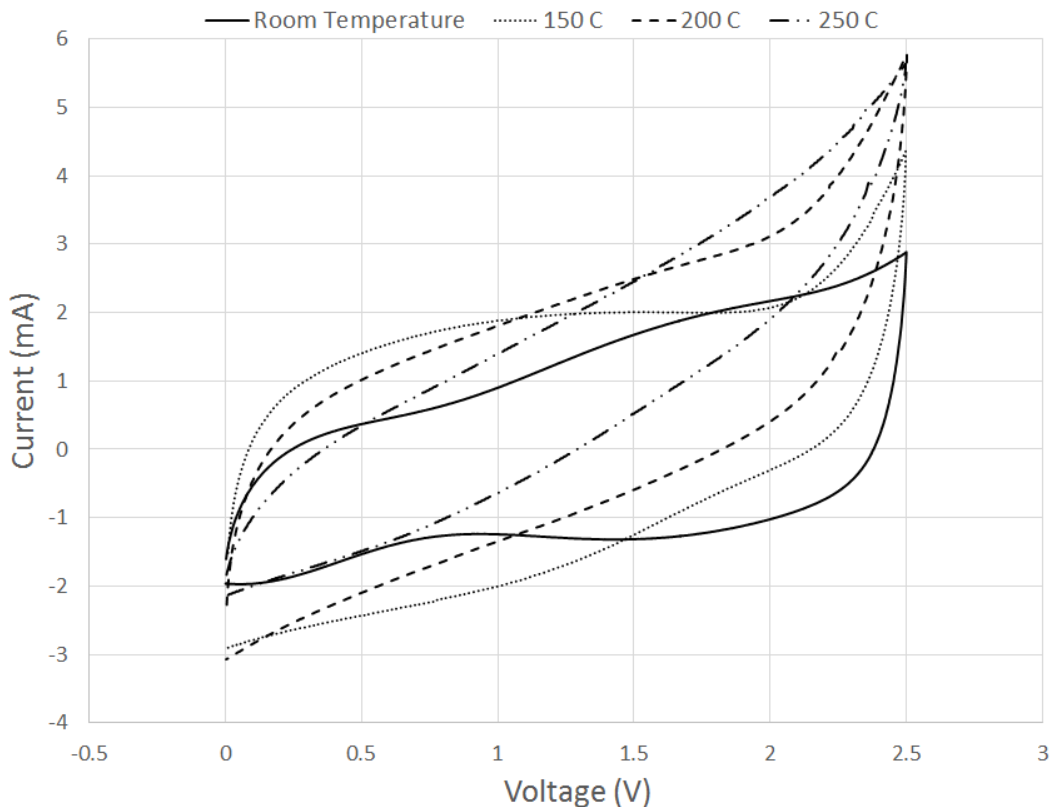


Fig. 8 CV plots from a single device, measured at RT, and 150, 200, and 250 °C with [BMIM][BF₄] IL, taken at 0–2.5 V and 100 mV/s. Capacitances for these temperatures were 87, 122, 105, and 68 F/g for a-d, respectively.

However, when a device has been heated and then returned to RT the performance degrades significantly. It is possible that the device was degraded during the heating process but this degradation was counteracted by an increase in conductivity of the IL. It is also possible that the device was somehow damaged during cooling. So while these devices have been demonstrated at high temperatures, high/low temperature cycling appears is problematic at this point.

To visualize the energy storage potential of these devices, the energy densities are plotted versus power densities to create a Ragone plot (Fig. 9). To produce this plot,

charge/discharge measurements were made at different charge rates with the same device, at RT, and at 200 °C. The RT test returned a typical Ragone plot, with energy density decreasing as power density increases. At higher temperatures, we see that energy and power density increase significantly as compared to the RT test, but the values quickly fall off as we go towards lower power densities. During the test, it was observed that at lower current rates, the device would not charge up to the full voltage for the test in the allotted time, and so the achieved energy densities were diminished due to the lower energy stored at lower maximum voltages. While this is essentially an artifact of the measurement, it does point to a real limitation in the device at elevated temperature.

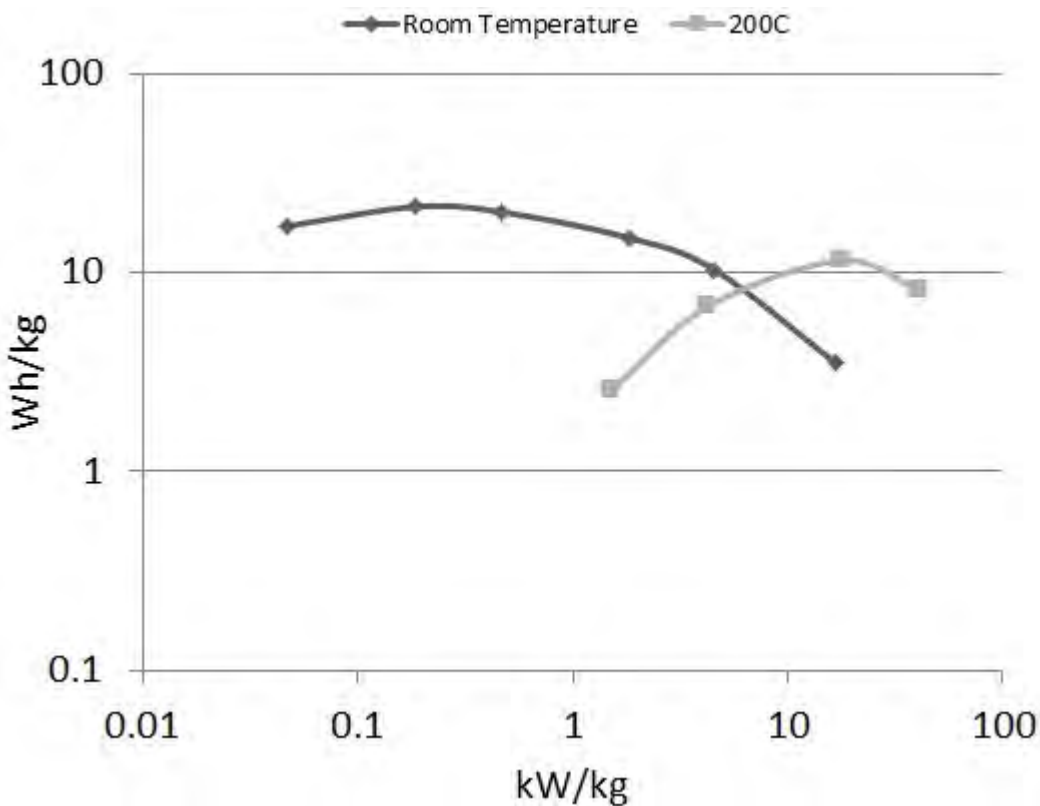


Fig. 9 Ragone plot of a device with [BMIM][BF4] electrolyte, tested at charge rates between 0.025 and 25 A/g, showing that the power and energy densities increased with temperature. Though, the leakage current of the devices at higher temperatures (Fig. 11) prevented the device from charging fully at lower charging rates, resulting in lower energy densities (the two leftmost data points for the 200 °C measurements).

The lack of charging to the programmed voltage is attributed to the leakage current of the device. This is a vitally important characteristic as it determines how well the supercapacitor can store charge over a period of time. We tested leakage current at RT and at 200 °C with [BMIM][BF4] electrolyte devices (Fig. 10). At RT, the devices performed much better than at 200 °C, where self-discharge of the cells

was unacceptably large. This is the most significant challenge for making these high temperature devices, and more study will be required to determine the self-discharge mechanism and whether more suitable electrolytes can be obtained.

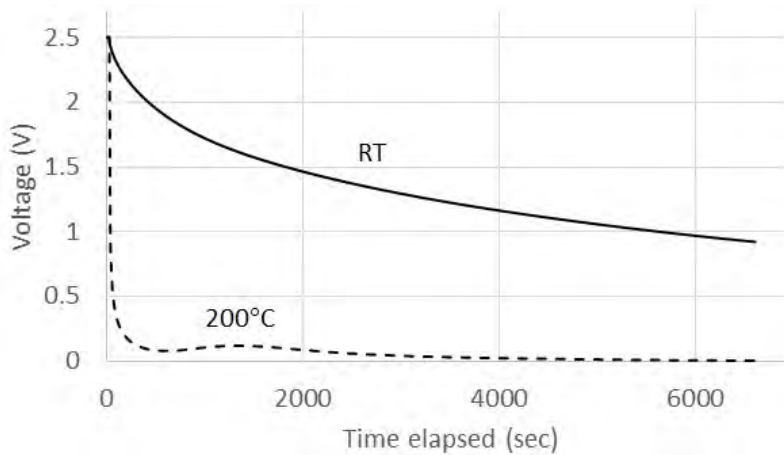


Fig. 10 Self-discharge test of devices as tested at RT (solid) and 200 °C (dashed). Devices are held at 2.5 V for 10 min to ensure that the device is fully charged, then the circuit is opened and the voltage change is measured as the supercapacitor self-discharges. The ability for the device to store charge is greatly diminished at high temperatures.

While testing these flexible devices, it was noticed that the devices tested at elevated temperature had better cycle life than those tested at RT (Fig. 11). This could be attributed to reducing the adverse effects of any water in the cell by keeping the device above 100 °C. It is known that Kapton is permeable to water (Ervin et al. 2014), and the life-cycle tests take approximately 28 h to run, so in an ambient environment it is possible that the cells are absorbing water, which would reduce performance. If water is in the cells, it can fill electrode pores with gas due to electrolysis at the higher potentials used with the IL electrolytes. This would block access of the IL to some of the electrode surface area, reducing capacitance. Another potential degradation mechanism includes the breakdown of the [BMIM][BF₄] IL. Byproducts of [BMIM][BF₄] decomposition, in the presence of water, include hydrogen fluoride (HF), which could negatively affect the current collector and graphene interface.

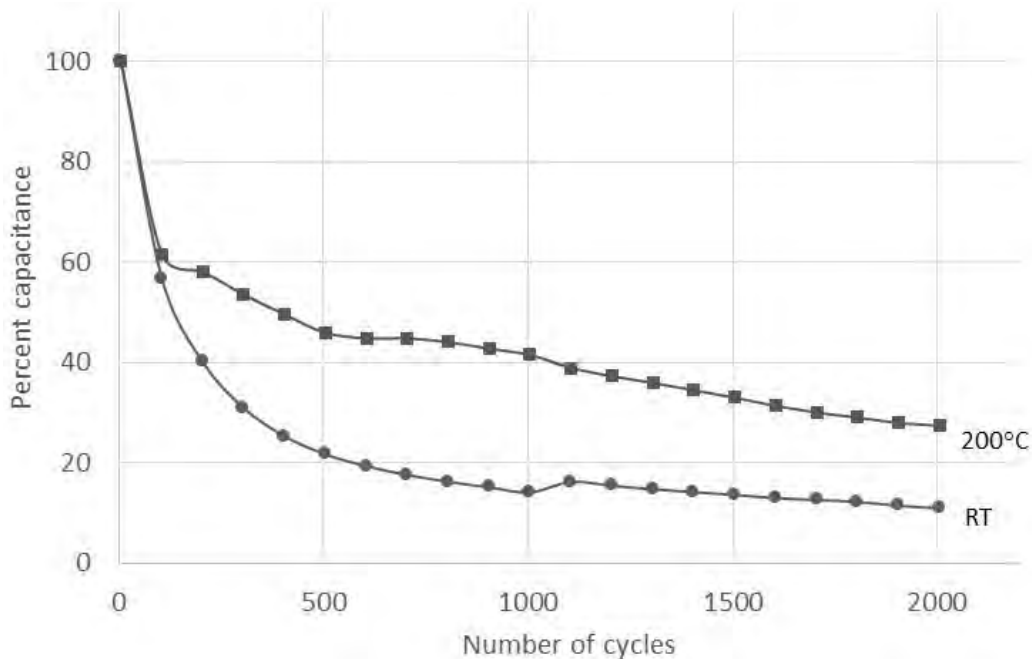


Fig. 11 Cycle life comparison of devices tested at 200 °C and RT. The plotted results are the averaged results for 3 devices at each temperature. Capacitance is higher at elevated temperatures. CV tested at 100 mV/s, from 0.0 to 2.5 V. These devices are identical: steel current collectors and [BMIM][BF₄] electrolyte.

To try and confirm if water, or some other atmospheric contamination such as oxygen, is affecting device performance, tests were carried out with devices sealed in hermetic packaging material immediately after processing. The packaging used was Bemis Shield Pack Class poly(o-phenylenediamine) (PPD) film, which is heat sealed for good water resistance, but does not have a high operating temperature. These devices and similar non-hermetic Kapton devices were placed on a countertop in an environment of approximately 50% humidity for 1 week before testing. We found that the hermetically sealed devices performed much better than those sealed only in Kapton, when tested at RT. Devices that were sealed in PPD film had higher overall capacitance, even though the decay rates were fairly similar to the Kapton-only devices (Fig. 12).

We also created devices that were sealed in aluminum (Al) tape, which offers a water tight seal while having higher operating temperatures than the PPD film. These devices could be tested in the oven at 130 °C. Again, these devices and a comparison devices, packaged only in Kapton, were left to sit on a countertop for 1 week before testing. When CV measurements were made at 130 °C, the degradation of the devices was similar (Fig. 13). It is possible that any water that had accumulated in the Kapton-only cell evaporated when heated in the oven and prevented any adverse effects during cycling.

In other similar devices, we observed that RT self-discharge currents were lower for hermetically sealed devices, but above 100 °C the sealed and unsealed devices performed similarly. Whether the observed difference is due to water being driven off above 100 °C or increased self-discharge currents due to other leakage current mechanisms dominating at higher temperatures, is not clear.

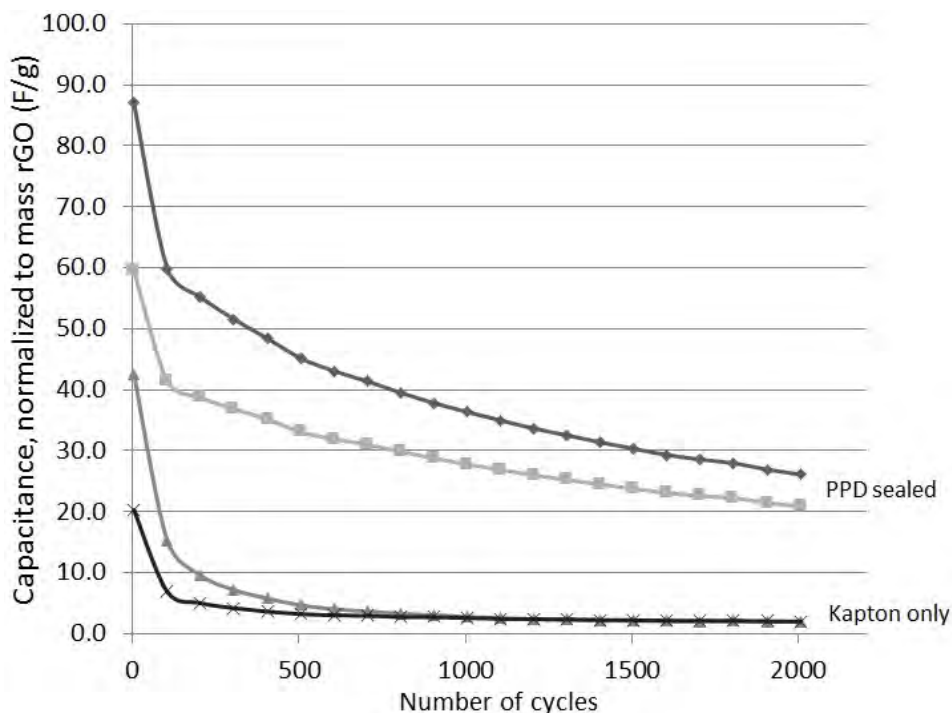


Fig. 12 Cycle life tests for 2 devices sealed in PPD and 2 Kapton-only devices are left in ambient air for 1 week to absorb water. The devices are otherwise similar with steel current collectors and [BMIM][BF₄] electrolyte. Capacitances are higher for the devices that have been hermetically sealed. These devices were CV tested at RT at 100 mV/s from 0–2.5 V.

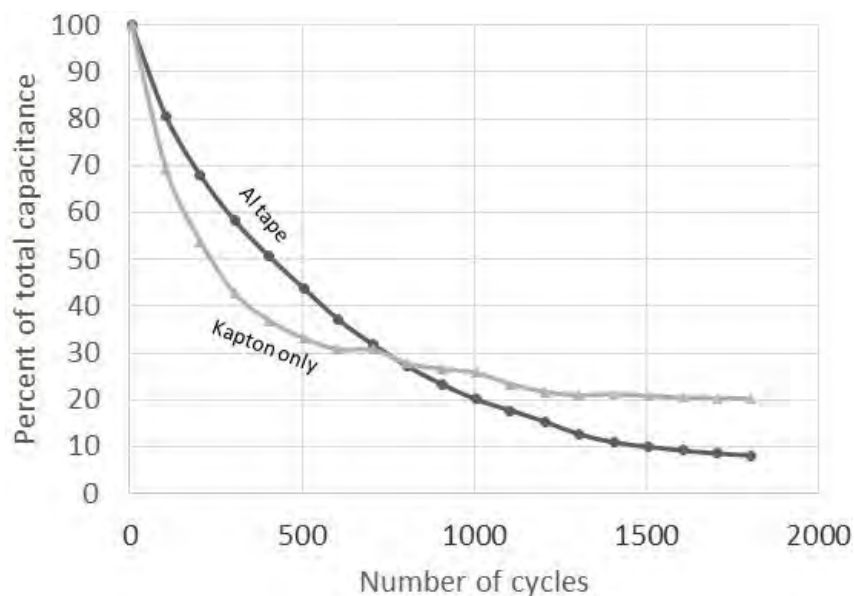


Fig. 13 Cycle life tests of Al tape hermetically sealed and Kapton only non-hermetically sealed devices tested at 130 °C. The sealed and unsealed devices have similar performance, in contrast to the RT tests. Any water in the non-sealed package may be evaporating out of the cell, eliminating adverse effects. These devices were CV tested at 100 mV/s from 0–2.5 V with [BMIM][BF₄] electrolyte.

Though hermetic sealing proves to be effective in extending the performance, the life cycles of the [BMIM][BF₄] devices are still relatively poor, decaying to <40% after 2000 cycles when tested at RT, and <20% when tested at 130 °C. Therefore, another electrolyte was investigated to see if it improves life-cycle performance, especially if the adverse effects were caused by HF formation or because of the hydrophilic properties of the [BMIM][BF₄]. This alternative IL, EMI-DCA (Huang et al. 2015) is hydrophobic, as compared to the hydrophilic [BMIM][BF₄], and so it should resist infiltration of water into the device. In addition, it does not contain any fluorine, so HF is no longer a potential decomposition product that could negatively affect the devices. We revisited the need for a wet anneal with this electrolyte in order to validate the claims of Huang et al. (2015) that sufficient wetting is achieved at RT. As seen in Fig. 14, the devices made with this electrolyte performed very close to each other regardless of whether they were wet or dry annealed, though the dry annealed devices took around 300 cycles before reaching peak capacitance (as shown by the capacitance starting low and growing in Fig. 14). Whereas the electrolyte permeated the rGO with the wet anneal processing, the dry annealed electrode apparently needs to electro-wet before achieving capacitance values similar to the wet anneal counterparts. We see that when the device is tested again (at 130 °C), this burn in period no longer occurs. We also observed that these devices do not necessarily need to be sealed to keep out water, performance was similar performance between sealed and unsealed

devices in our tests, indicating that the hydrophobic nature or lack of fluorine may be significant advantages. This EMI-DCA electrolyte appears to have a number of advantages since it does not need a wet anneal, and it also has less stringent packaging requirements since water-tight packaging is not necessary. Unfortunately, the life-cycle decay seems to be similar to the [BMIM][BF₄], decaying to less than 20% over 2000 cycles.

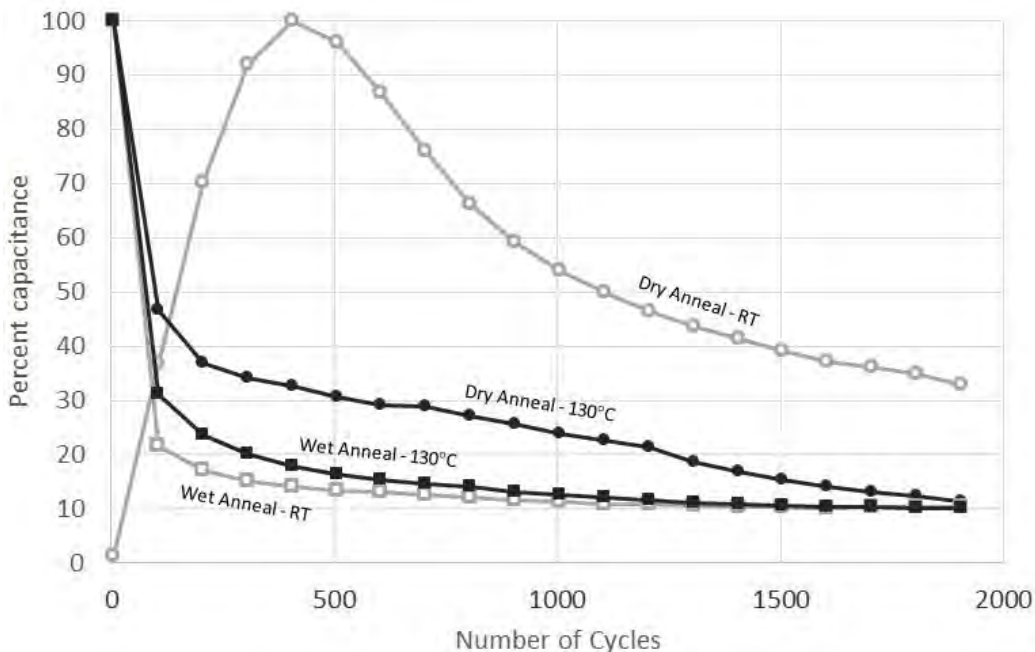


Fig. 14 Cycle life tests of flexible devices made with EMI-DCA electrolyte, testing the difference in performance between dry and wet anneal procedures. These devices were tested at RT and then at 130 °C, at 100 mV/s, from 0–2.5 V with the results of each test normalized to the peak capacitance measured. The devices had similar life cycle decay, independent of dry or wet anneal.

5. Summary and Conclusion

This work demonstrated the optimal anneal temperatures for 3 methods of thermal anneal to reduce GO and wet it with IL electrolyte: 200 °C for dry anneal, 200 °C for dry/wet anneal, and 220 °C for a wet anneal. In most of the literature found, the dry anneal procedure is the only method used, but we obtained only poor performance using this procedure with ILs such as [BMIM][BF₄]. With the development of 2 new procedures, dry/wet and wet anneal, better performance was achieved with the [BMIM][BF₄] IL. While the wet anneal produced superior capacitance to the dry/wet anneal, the ability to potentially use lower temperatures in the dry/wet anneal procedure may be useful for situations where low temperature processing is required. The addition of a solvent such as DMF, or use of an alternative IL such as EMI-DCA, proved to be useful as well in this respect. The

presumed mechanism for these IL wet annealing procedures relates to the viscosity of the permeating electrolyte: as the liquid is heated, or the viscosity is decreased by a solvent, it can better wet the electrodes.

Using the wet anneal technique for the thermal reduction of GO with IL enabled the creation of flexible, high operating temperature devices. We have shown that devices made with this procedure have significant capacitance (up to 100 F/g) at the thermal limits of the cell (over 200 °C). We also showed that sealing of these devices in hermetic packaging will increase the performance of the devices by keeping out contaminants that can permeate through the Kapton packaging. Outstanding issues with these devices are poor cycle life and elevated temperature self-discharge, which indicate that there is still significant work to be done to determine and defeat the degradation and self-discharge mechanisms in order to develop a practically useful flexible supercapacitor that operates in the 150 to 250 °C range.

6. References

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List of Symbols, Abbreviations, and Acronyms

[BMIM][BF ₄]	1 butyl-3-methyl-imidazolium tetrafluoroborate
Al	aluminum
C	carbon
Cr	chromium
CV	cyclic voltammetry
DI	deionized
DMF	dimethylformamide
EIS	electrochemical impedance spectroscopy
EMI-DCA	1-ethyl-3-methylimidazolium
FEP	fluorinated ethylene propylene
GO	graphene oxide
HF	hydrogen fluoride
IL	ionic liquid
K ₂ SO ₄	potassium sulfate
Ni	nickel
O	oxygen
PPD	poly(o-phenylenediamine)
Pt	platinum
rGO	reduced GO
RT	room temperature
SL	single-layer
Ti	titanium

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RDRL CIO LL TECHL LIB
- 1 GOVT PRNTG OFC
(PDF) A MALHOTRA
- 3 US ARMY RSRCH LAB
(PDF) RDRL SER L
L LEVINE
M ERVIN
B PIEKARSKI