Flexible reduced graphene oxide supercapacitors processed using atmospheric-pressure plasma jet under various temperatures adjusted by flow rate and jet-substrate distance

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Abstract
We vary the substrate temperature by adjusting the nitrogen flow rate and jet-substrate distance during nitrogen atmospheric-pressure plasma jet (APPJ) processing of screen-printed reduced graphene oxides (rGos) on carbon cloth. The APPJ-processed rGos on carbon cloth are then used as electrodes for supercapacitors. Increasing the nitrogen flow rate could reduce the gas temperature and enhance the reactivity of the reactive plasma species. Typically, lowering the temperature slows down the chemical reaction; however, increased reactivity of the reactive plasma species at the same jet-substrate distance could compensate the temperature effect. A nitrogen APPJ could improve the wettability of the screen-printed rGos on carbon cloth. We found that 20-s APPJ treatment increases the areal capacitance from 6.2 mF cm\(^{-2}\) (without APPJ treatment) to 22.4 mF cm\(^{-2}\) (700 °C, 30 slm), as evaluated by galvanostatic charging/discharging (GCD) measurements under a constant current of 0.25 mA. Further, 20-s nitrogen APPJ processing at temperatures of ~600 °C–700 °C could obtain the best areal capacitance value. The capacitance value of the fabricated flexible rGO supercapacitor remains at similar level after 1000-cycle mechanical bending test with a bending radius of 5 mm.

1. Introduction
The atmospheric pressure plasma (APP) is generated without using vacuum chambers and pumps [1]. Therefore, it is particularly feasible to integrate with the fabrication processes of devices that are typically fabricated in a non-vacuum environment. APP technology is used in many applications such as material surface treatment [2, 3], agriculture and medicine [4–6], and nanomaterial syntheses [7, 8]. Various types of APP technology have been developed; one such example is jet-type APP, also called atmospheric-pressure plasma jet (APPJ). In an APPJ, the plasma is generated inside a jet and is brought out of the jet by a high speed jet flow. The flow also cools and stabilizes the APP to prevent continuous arc generation. When using an APPJ for performing chemical reactions or material treatment, several factors such as temperature and plasma reactivity could influence the chemical reaction. APPJ can be used as a rapid thermal processing tool with low energy consumption. The energy consumption is estimated to be about 1/3–1/5 of that by using a conventional electric furnace [9, 10]. Because APPJ is operated in atmospheric pressure, the gas phase byproducts during rapid thermal processing can be easily vented without contaminating the equipment. By contrast, if a rapid infrared furnace is used, the gas byproducts can possibly contaminate the quartz tube or gold reflector. In addition,
Table 1. Combinations of quartz tube lengths and flow rate for various substrate surface temperatures during APPJ operation.

| Substrate surface temperature | Quartz tube length | Flow rate |
|-------------------------------|-------------------|-----------|
| 450 °C                        | Long tube (6.2 cm) | 48 slm    |
| 500 °C                        | Long tube (6.2 cm) | 45 slm    |
| 600 °C                        | Short tube (4.7 cm) | 37 slm    |
| 700 °C                        | Short tube (4.7 cm) | 30 slm    |

compared with low pressure plasma, APP is easier to integrate into roll-to-roll fabrication processes. The synergetic effect of reactive plasma reactive species and heat offers rapid processing capability. The materials processing can be speeded up at lower temperature by the assistance of reactive plasma species.

Supercapacitors, having high capacitance value but low applied voltage, are extensively used for rapid charging-discharging and high power density purposes. The major mechanisms are electrical double layer and pseudocapacitance. Carbon is the most extensively used material for commercial supercapacitors and much research effort has been based on supercapacitors to develop energy storage device with higher power density, higher energy density, and deformability. Meng et al used plasma treatment to enhance electrochemical performance of graphene fiber-based supercapacitors [11]. Park et al designed and fabricated a stretchable microsupercapacitors based on reduced graphene oxide (rGO)-Au heterostructures patterned by direct laser patterning [12]. Liu et al used microplasma jet etching to define patterns on coplanar CNT microsupercapacitors without masks [13]. Chodankar et al used nitrogen plasma to dope nitrogen into carbon fibers of carbon cloth, leading to an high areal capacitance of 741 mF cm⁻² [14]. Zhang et al reported that supercapacitors with high areal capacitance have been realized using hierarchical carbon tubular nanostructures [15]. Kuok et al used DC-pulse nitrogen APPJs to process CNT-rGO electrodes for supercapacitors with processing time within 30 s [16, 17].

In recent years, we have tested the use of a nitrogen DC-pulse arc APPJ in many materials processes [9, 16–18]. In these experiments, the plasma reactivity at the surface of the material being treated was found to be related to the input power and the decay process of plasma reactive species. A higher flow rate reduces the temperature but increases the plasma reactivity when reaching the material with a fixed jet-substrate distance [19–21]. By contrast, a shorter jet-substrate distance could lead to higher temperature and higher reactivity of the plasma species. Previously, we have fabricated flexible reduced graphene oxide (rGO) supercapacitors by applying an APPJ activation process to rGO-coated carbon cloth [17, 21, 22]. In this study, we further adjust the processing temperature by the varying flow rate and jet-substrate distance; the input power is not varied to avoid plasma instability. We found that 20-s nitrogen APPJ processing at temperatures of ~600 °C–700 °C could obtain the best areal capacitance for supercapacitors with APPJ-activated rGO-coated carbon cloth. Further, we demonstrate, for the first time, preliminary cyclic mechanical test results for APPJ-processed flexible rGO supercapacitors.

2. Experimental details

2.1. Fabrication of flexible supercapacitors

The preparation procedures of the rGO pastes and the gel-electrolyte solutions are described elsewhere [22]. The rGO pastes were screen-printed on a carbon cloth (W051002, without a microporous layer and polytetrafluoroethylene, CeTech Co. Ltd) with an area of 1.5 cm × 2 cm. After screen-printing, the rGO-coated carbon cloth was baked at 100 °C for 3 min using an electric furnace. A DC-pulse nitrogen APPJ was used to treat the rGO-coated carbon cloth for 20 s. The APPJ setup is described elsewhere [22]. Various flow rates and a quartz tube with various lengths were used to adjust the substrate surface temperature during APPJ operation. Table 1 lists the combinations of flow rate and quartz tube length for various temperatures. Figure 1 shows the time course of the substrate surface temperature measured using a K-type thermocouple. The plateau of temperature was adjusted to 450, 500, 600, and 700 °C by varying the combinations of flow rate and jet-substrate distance (quartz tube length). Because of the convective cooling effect, for a fixed jet-substrate distance, the higher the flow rate, the lower is the substrate surface temperature. Increasing the jet-substrate distance also lowers the temperature. After APPJ processing, a polyvinyl alcohol (PVA)/H₂SO₄ gel-electrolyte solution was spread on the rGO-coated carbon cloth and dried naturally. This gel-electrolyte coating procedure was repeated three times. Finally, two pieces of gel-electrolyte coated rGO carbon cloth were pressed on the gel-electrolyte sides to form a sandwich-type supercapacitor. Figure 2 shows the fabrication process of the flexible rGO supercapacitors.
2.2. Characterization of supercapacitors

The surface morphology of the rGO-coated carbon cloth was inspected using a scanning electron microscope (SEM, JSM-7800F Prime, JEOL). The water contact angle was measured using a goniometer (Model 100SB, Sindetake). Galvanostatic charging/discharging (GCD) measurements were performed using an electrochemical workstation (Metrohm Autolab) at constant currents of 0.2, 0.4, and 0.6 mA with a potential window of 0–0.8 V.

Figure 1. Time courses during APPJ operations: (a) 450 °C, 48 slm; (b) 500 °C, 45 slm; (c) 600 °C, 37 slm; and (d) 700 °C, 30 slm.

Figure 2. Schematic diagram of fabrication process of flexible rGO supercapacitors.
3. Results and discussion

3.1. Water contact angles of rGO-coated carbon cloth

Figure 3 shows the water contact angles of the rGO-coated carbon cloth before/after APPJ processing. Without APPJ processing, the rGO-coated carbon cloth exhibits a high contact angle of 121.9°; after APPJ processing, for all temperatures, the rGO-coated carbon cloth becomes hydrophilic and the tested water droplet completely penetrates into the rGO-coated carbon cloth. This agrees with our previous results [22]. In our previous study, x-ray photoelectron spectroscopy shows that APPJ treatment can introduce –COOH function groups and nitrogen doping to rGO-coated carbon cloth. These could lead to the improved wettability [21]. It is noted that APPJ treatment also burns out ethyl cellulose (which contains large amount of –OH) in the pastes, and therefore, the overall –OH content is reduced [21]. The improved wettability can facilitate contact between the gel-electrolyte and the rGO-coated carbon cloth, thereby improving the capacitance value, as shown later.

3.2. Surface morphology of rGO-coated carbon cloth

Figure 4 shows SEM images of the rGO-coated carbon cloth before/after APPJ processing. The rGO pastes also contain ethyl cellulose (EC) as binders. EC is more vulnerable to nitrogen APPJ than rGO nanosheets. Nitrogen APPJ quickly burned out the EC but also partially damaged the rGO nanosheets [9, 23]. As seen in figure 4(a), the flake-like rGOS are surrounded by ECs. After APPJ treatment, as seen in figures 4(b)–(d), some sharp edges of rGOS revealed. The exposure of rGOS can have better contact with the gel-electrolyte, thereby increasing the capacitance value as described latter. APPJ treatment for an overly long duration may completely burn out the rGOS [21, 24]. Therefore, in this study, the APPJ processing time is limited to 20 s. Abundant rGOS are still
present after APPJ processing at all temperatures. As shown in figure 4, sharp edges are seen after APPJ processing because of the burnout of ECs and partial damage of rGO nanosheets.

3.3. GCD characterization of rGO supercapacitors

Figure 5 shows the GCD results for rGO supercapacitors. With higher APPJ temperature, the charging-discharging time increased, indicating increased capacitance. The areal capacitance $C_A$ can be calculated based on \[ C_A = \frac{4I \cdot T}{A \cdot \Delta V} \] (1)

where $I$ is the discharge current; $T$, the discharging time; $\Delta V$, the potential window; and $A$, the apparent area of the two electrodes. Table 2 lists the calculated areal capacitance based on figure 5. We found that 20-s APPJ treatment increased the areal capacitance from 6.2 mF cm$^{-2}$ (without APPJ treatment) to 22.4 mF cm$^{-2}$ (APPJ treatment under 700 °C, 30 slm). The improved hydrophilicity after APPJ treatment may facilitate the contact between the gel-electrolyte and the rGO-coated carbon cloth, thereby increasing the areal capacitance value. APPJ burned out ECs to expose rGOs could also lead to the improved capacitance value. The improvement in areal capacitance becomes apparent with increased temperature and decreased flow rate. Increasing the flow rate (lower temperatures) may improve the reactivity of the plasma reactive species reaching the rGO-coated carbon cloth. By contrast, increasing the temperature typically increases the chemical reactivity. These two factors compensate each other. In our experimental cases, the situation is complicated because short tube is used for high-temperature cases (600 °C and 700 °C). A shorter jet-substrate distance also makes the plasma reactive species more reactive while reaching the rGO-coated carbon cloth because less quenching effect occurs in their

![Figure 5. Comparison of GCD curves of rGO supercapacitors treated by APPJ under various conditions (No APPJ treatment; APPJ treatment under 450 °C, 48 slm; APPJ treatment under 500 °C, 45 slm; APPJ treatment under 600 °C, 37 slm; and APPJ treatment under 700 °C, 30 slm).](image)

| APPJ treatment condition | GCD constant current 0.25 mA | GCD constant current 0.5 mA | GCD constant current 1 mA |
|--------------------------|-------------------------------|-------------------------------|----------------------------|
| No APPJ treatment        | 6.20                          | 4.7                           | 3.8                        |
| APPJ treatment under 450 °C, 48 slm | 13.51                        | 12.88                         | 12.68                      |
| APPJ treatment under 500 °C, 45 slm | 13.93                        | 13.22                         | 12.77                      |
| APPJ treatment under 600 °C, 37 slm | 18.79                        | 18.15                         | 17.6                       |
| APPJ treatment under 700 °C, 30 slm | 22.43                        | 21.73                         | 21.16                      |

Unit: mF/cm$^2$
transport path. The experimental results show that the improvement in capacitance is positively correlated with the temperature. This could imply that temperature is the major factor to improve the areal capacitance values because of the burnout of ECs and activation of rGOs; plasma reactive species could play a complementary role in speeding up the reaction. To ensure the reproducibility of the results, we repeated the experiment three times. Figure 6 shows the GCD areal capacitance results of the three batches of samples. The results are very consistent and we find that the areal capacitance achieves a higher value for APPJ treatment at \( \sim 600 \text{ }^\circ\text{C} - 700 \text{ }^\circ\text{C} \).

### 3.4. Cyclic mechanical bending test of flexible rGO supercapacitors

We further test the mechanical stability of the flexible rGO supercapacitors. A 3D-printer is used to fabricate a bending test module, as shown in figure 7. The bending radius is set to 5 mm. We performed 1000 bending cycles and measured the areal capacitance every 200 cycles. Figure 8 shows the areal capacitance value versus the number of bending cycles. After 400 cycles, there is a small decrease in capacitance value, around 1 mF cm\(^{-2}\) out of \( \sim 27 \text{ mF cm}^{-2} \). It could be within the error margin. The other possibility is the equilibration of the electrode potential \[26\]. Once the system is stabilized, the capacitance remains in similar level in the next 600 cycles. Overall, the results show merely slight variations in the areal capacitance value and the flexible supercapacitor remained functional with comparable areal capacitance value to that of a supercapacitor before bending test.

### 4. Summary

APPJ-processed rGO-coated carbon cloth is used as the electrode of a PVA/H\(_2\)SO\(_4\) supercapacitor. Combinations of various flow rates and jet-substrate distances are used to adjust the substrate temperature under APPJ operation. APPJ treatment significantly improves the wettability of the rGO-coated carbon cloth and thereby facilitates contact between the gel-electrolyte and the electrodes. This, in turn, increases the areal capacitance value. 20-s APPJ treatment increases the areal capacitance from 6.2 mF cm\(^{-2}\) (without APPJ treatment) to 22.4 mF cm\(^{-2}\) (700 \text C, 30 slm), as evaluated by GCD under a constant current of 0.25 mA.
Further, 20-s nitrogen APPJ processing at temperatures of $\sim 600 ^\circ C$–$700 ^\circ C$ realizes the best areal capacitance value. Our experimental results suggest that temperature plays the main role and plasma reactive species play a complementary role in activating rGO-coated carbon cloth. The fabricated flexible rGO supercapacitor shows good mechanical stability under a 1000-cycle mechanical bending test with a bending radius of 5 mm.

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Figure 8. Areal capacitance of flexible supercapacitors after cyclic bending under a bending radius of 5 mm. The sample was made under APPJ condition of 700 °C and 30 slm flow rate.
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