Plasma Enhanced Chemical Vapor Deposition Reactor for Large-Scale Production of High Quality Graphene

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ABSTRACT

Combining graphene with bulk materials holds great promise for advancing and developing defence technologies. As an additive, flake graphene gives high strength to weight and can impart enhanced mechanical, thermal, and electronic properties to polymers even at very low concentrations. As continuous thin film or coating, graphene can be applied to a wide range of materials, providing a flexible, transparent, electrically conductive, corrosion resistant, gas impenetrable and atomically thin diffusion barrier. However, a challenge with graphene is producing high quality on large scale.

Here, we present a large-scale Plasma Enhanced Chemical Vapour Deposition, PECVD, reactor system, FORZA, that has been developed exclusively for the large-scale production of high-quality graphene flakes and coatings. The reactor system is the largest known system of its kind, and can coat large surfaces, up to 86 cm width and 390 cm length, with vertically arranged graphene. FORZA is capable of large area graphene coating or the graphene is harvested continuously as a powder.

Some of the applications utilizing graphene are presented. These are including conducting polymers, strengthened epoxies and elastomers, and coating of various materials. We are also showing possibilities for boosting battery charging performances.

1.0 INTRODUCTION

Defence applications of graphene-based materials are numerous. As an example, these materials may be used as anti-corrosion and anti-icing coatings for helicopters rotor blades. Moreover, graphene-based materials are believed to provide high strength-to-weight ballistic solutions for vehicles and body armour. There are also great possibilities with enhancement of battery's energy density and rate performance with the use of graphene. Although the potential of graphene has been highlighted in numerous laboratory studies, there are still challenges in producing graphene with sufficient quality and scale necessary for industrial applications. The FORZA machine has shown that these hurdles can be overcome, and it is used both as a research reactor for determining properties for new specialized coating machines, as well as serving as a graphene production machine.

Current methods for producing flake graphene are based on top-down exfoliation of graphite by either mechanical or chemical means. Techniques, such as the Scotch-tape method or shear-force mixing, can produce high quality graphene flakes with little contamination, but are limited to small productions volumes. Chemical exfoliation can produce a higher volume of graphene than mechanical exfoliation, but the process is harsh and results in substantial damage and undesirable effects to the graphene itself including defects, oxide functionalities, substitutional nitrogen, and residual metallic contaminants. Chemical waste is also an issue with chemical exfoliation.

High quality graphene films can be produced by chemical vapor deposition (CVD). CVD of graphene is a bottom-up process whereby gaseous hydrocarbons are converted to crystalline graphene via high temperatures and catalytic substrates. Although thermal CVD is capable of producing high quality graphene films, the trade-offs include the need for high temperatures, ~1000 °C, slow growth times, and a limited number of substrates on which is can be applied. Plasma Enhanced CVD (PECVD) is a variant of thermal CVD wherein reactive growth species are generated within a plasma environment rather than with high temperatures. The advantages of PECVD include lower growth temperature, faster deposition, improved film quality, and the ability to deposit multilayer films. The high growth rates of PECVD allow graphene to be grown vertically from the substrate as opposed to regular CVD that only deposits horizontal layers. This makes it possible to grow substantially more graphene per growth area, that can easily be harvested to be used as flakes. However, a challenge with PECVD has been scaling the process to industrially relevant size.

The reactor system, FORZA, is based on a scalable microwave plasma technology platform. The system can transform carbon containing gases and continuously deposit vertical 3D graphene on areas of up to 6.7 m^2. Large-area graphene deposition has been demonstrated on a variety of substrates, including stainless steel, Inconel, aluminium, quartz, and copper, as well as more complicated structures, including metal mesh, carbon fibre cloth, and particles. Deposition can occur below 400 °C, which allows for coating of temperature sensitive materials and electronic devices. Characterization of FORZA flake graphene with scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy reveals excellent uniformity, high crystallinity and the morphology and size of the flakes. These properties can further be controlled by changing the growth conditions by varying the growth time, gas compositions, input energy, pressure, and temperatures.

2.0 METHODOLOGY

The FORZA machine (see Figure 2-1) was constructed as factor 6700 scale-up of the environment from a patented laboratory device set-up with a 1cm^2 growth area [1]. The corresponding growth areas in the FORZA machine consists of two 3.9 meter long metal bands where graphene can be vertically deposited either by dynamically moving the belts, or by step-static mode (see Figure 2-2). In this way it is possible to grow vertical graphene with different base length for the graphene sheets, which depending on residence time in the plasma zones, has been observed from a few hundred nm up to 30 µm thickness.

Figure 2-1: The FORZA graphene PECVD production unit at Cealtech in Stavanger, Norway

The produced graphene on the metal bands are harvested by mechanical scraping and pneumatic conveying from the reactor. In addition to controlling the flake sizes, the morphology of the produced graphene can be controlled by varying the process parameters, such as temperatures, total gas pressure, plasma energy, gas compositions, and argon dilution parameters. For on-line analysis, the machine has a probe installed for in-situ Raman spectroscopy measurements. In addition, there are routine inspection of harvested graphene powder by Raman mapping.

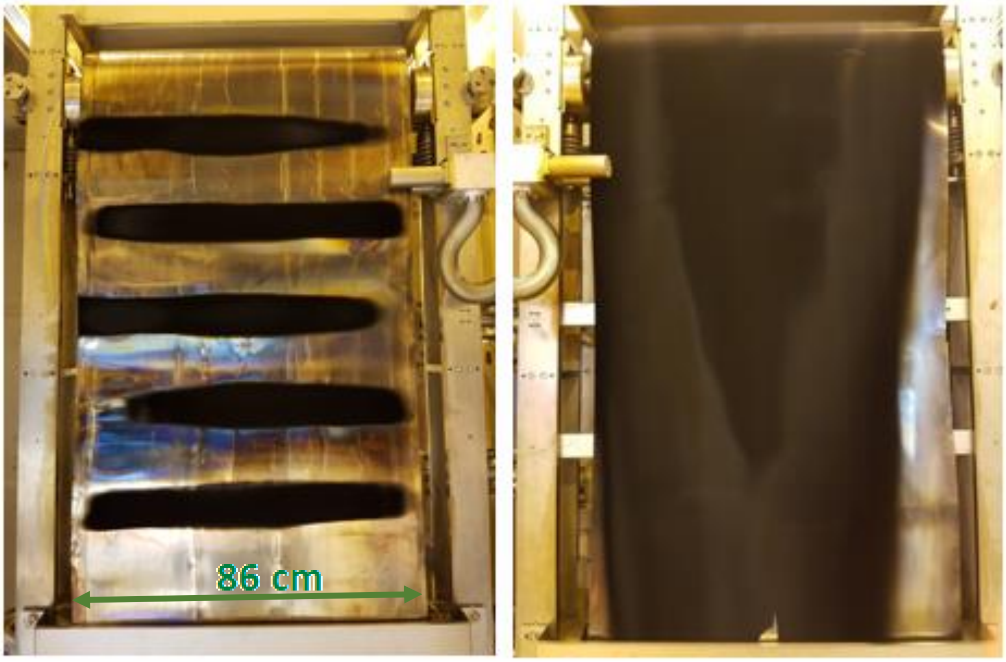

Figure 2-2: The graphene (black substance) inside the FORZA machine can be produced by different processing parameters, here is shown a step-mode growth (left) and dynamic mode growth (right)

Figure 2-3 show some of the obtained morphologies as shown by SEM. By TEM, and subsequent electron diffraction shows that the obtained graphene from the FORZA reactor is of high crystallinity and quality (See Figure 2-4).

The Raman spectra of neat FORZA graphene, Figure 2-5, and subsequent analysis, see Figure 2-6, shows that the produced graphene is very uniform. Furthermore, the neat graphene has a signature of being functionalized, which is believed to be hydrogenated graphene.

Figure 2-5 shows the spectrum before and after annealing the neat graphene in vacuum, and the resulting Raman spectrum looks more like pristine graphene. The neat FORZA graphene goes through interesting changes, where the most noteworthy is: low total mass losses of <28%; significant reduction of D and D’ peaks indicates reduction of defects (morphology and/or functionalization); the G peak width is maintained and indicates no deterioration of crystallinity. The great increase in the 2D peak area, and the 2D/G ratio, as well as a narrower 2D peak width from 78 to 61 cm^{-1}, indicates a reduction of over-all number of layers down to very few layers during the annealing process.

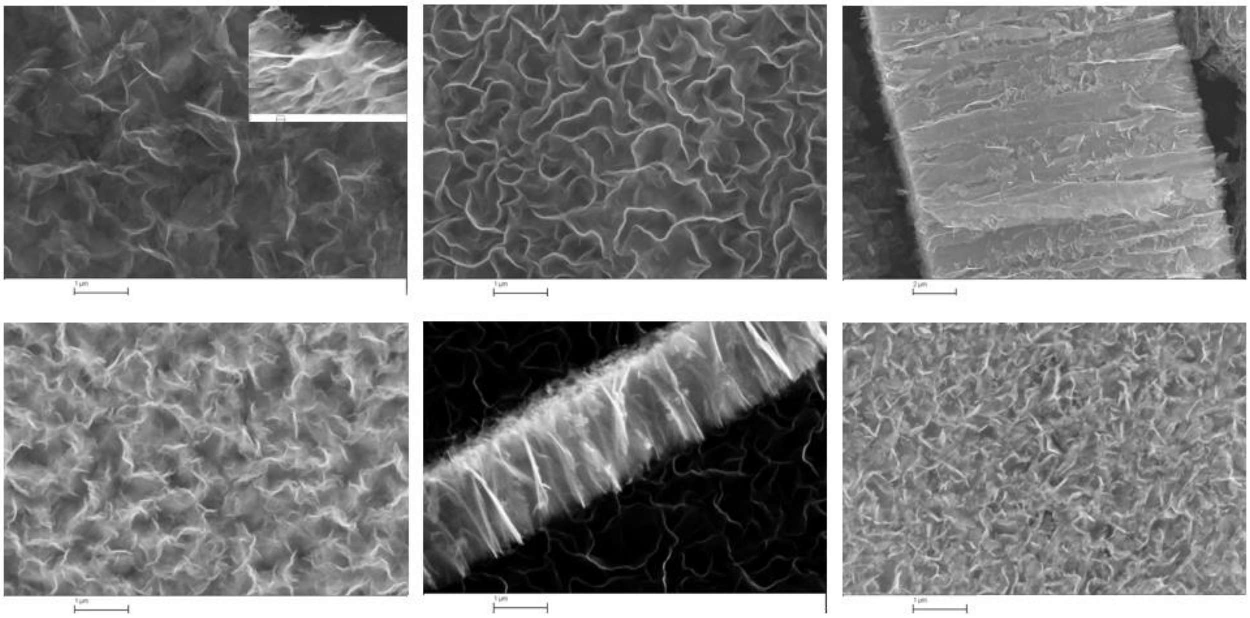

Figure 2-3: SEM pictures from the graphene morphologies that arise from tuning production parameters inside the FORZA reactor. By tuning gas compositions, temperatures and plasma power, different morphologies are grown. Here are shown wavy walls, maze like walls, dense structures, highly branched, loose branched morphologies.

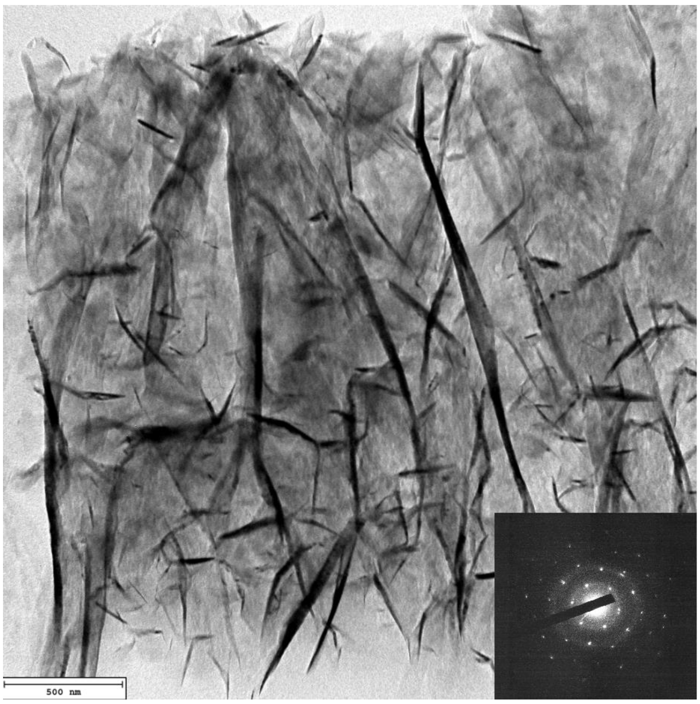

Figure 2-4: Transmission Electron Microscopy, TEM, images of a FORZA graphene flake. The indent at the bottom right shows the corresponding electron diffraction peaks from an arbitrary position in the TEM image. The diffraction pattern shows that the graphene has a high degree of crystallinity.

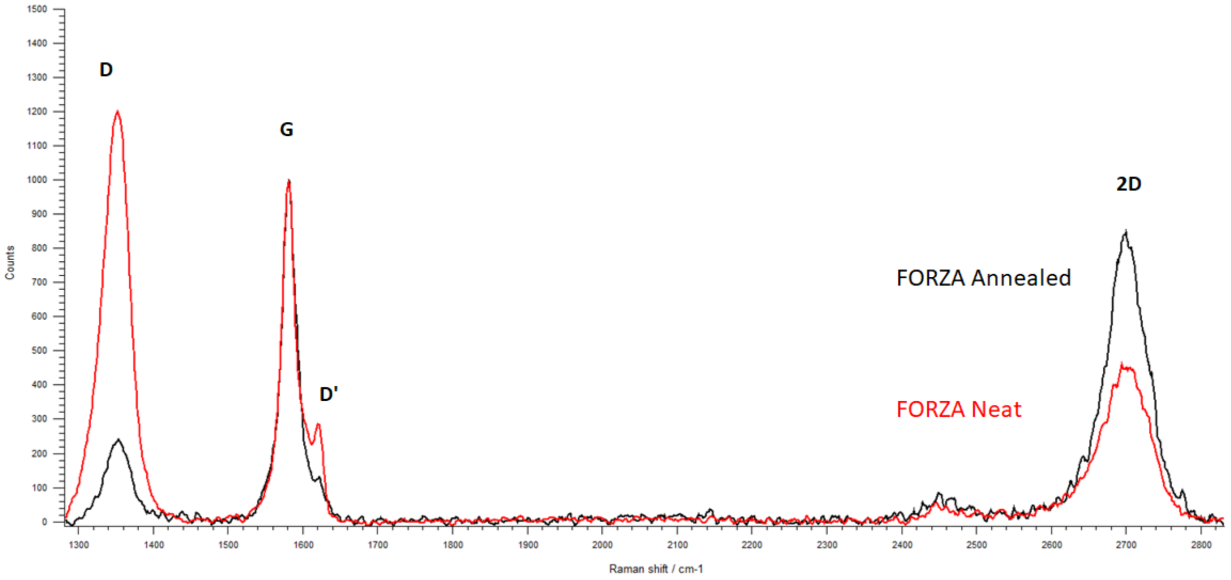

Figure 2-5: Raman spectra of FORZA graphene before and after heat treatment up to 1700 ˚C. For certain applications the neat Forza graphene is more useful for entering various material matrixes, while other applications can benefit from the properties of the annealed pristine version

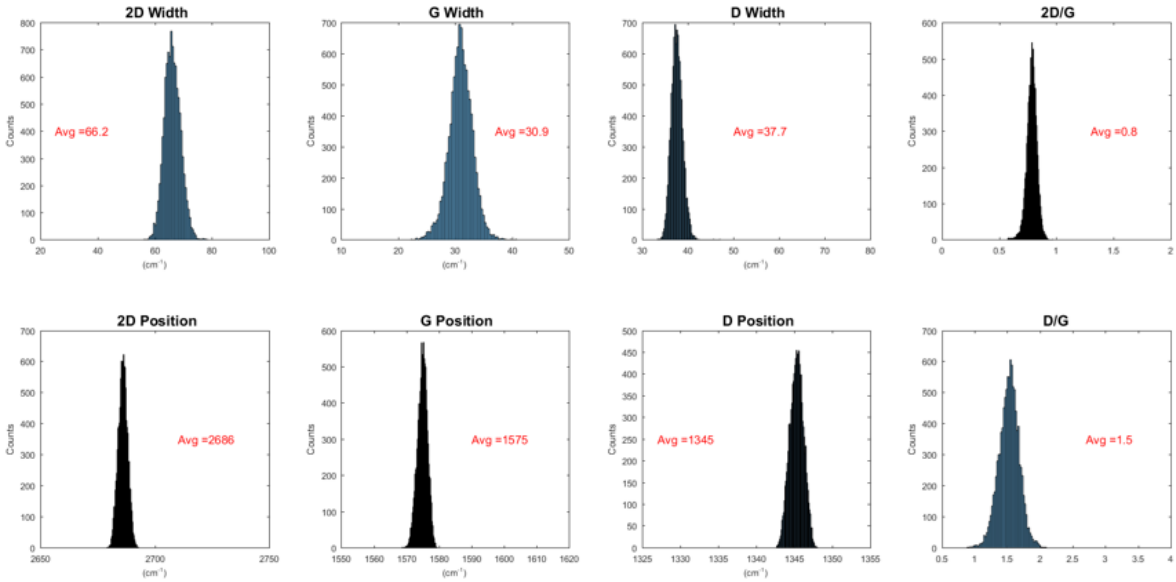

Figure 2-6: Distribution of Raman peak parameters and peak relations for a Raman map of neat FORZA graphene

Raman spectroscopy is a preferred tool for characterizing graphene in and from the production process and during subsequent manipulation for interfacing it in the various application matrixes. The Raman spectra and analysis give a good indication of the crystallinity and quality.

The morphology and nanostructure of graphene are routinely studied with SEM and TEM microscopy. In some cases, elemental composition is a necessary measurement, and can be looked at by e. g. x-ray photoelectron spectroscopy (XPS). Also x-ray powder- and or electron- diffraction can give valuable insight into qualities and dispersion of graphene.

For certain projects the properties such as conductivity, and material strengths are measured by standard methods.

3.0 RESULTS AND DISCUSSION

The FORZA graphene has been successfully applied in various polymer matrices, either as neat material or annealed or chemically functionalized, as well as mixed with other commercially available graphene. Some of the applications are of both military and commercial interests. In addition to powder material in the FORZA machine, it can be also used for direct large surface deposition of graphene on various materials. The only limit to direct deposition with the PECVD methodology is for the host material to sustain the conditions, such as temperature and low-pressure growth conditions.

Reinforcing advanced materials may be of military as well as commercial interest among others to reduce weight of various types of equipment such as stronger and lighter lifeboats. In addition, the altered electrical and thermal properties of graphene enhanced host matrix material may be beneficial for smart clothes as well as aiding anti-fouling and anti-icing properties of aviation machines.

Another area of interest is ballistic protection, and since graphene has shown to enter materials used as ballistic protection matrixes, there are projects ongoing, that aim at showing improvements of involved properties. The benefits obtained by increasing anti-ballistic performance are evidently lighter personnel equipment for soldiers/police officers, as well as lighter weight protection of vehicles.

3.1 Graphene enhanced fiber reinforced polyester

FORZA graphene was dispersed in fiber reinforced polyester and tested for increased performance (See Table 3-1). Tensile strength tests were performed according to the ASTM D3039 "Standard Test Method for Tensile Properties of Polymer Matrix Composite". Dimensions of specimen were: 200 x 25 x 10 mm [length x width x thickness]. Flexural strength (3-points flexure) test were performed according to ISO standard 14125 "Fiber-reinforced plastic composites – Determination of flexural properties".

All tests were performed on an Instron Applications Laboratory Model 5985. Test parameters such as loading speed and extensometers position were according to the ISO standards. For each sample, 7 specimens were tested to reduce uncertainty on the measurement.

Table 3-1: Increased strength performance of introducing FORZA vertical graphene into fibre reinforced polyester

Samples	Average Standard Tensile Strength (MPa)	*Increase compared to Ref (%)*	Average E-Modulus (MPa)	*Increase compared to Ref (%)*	Average Standard Maximum Flexure Stress (MPa)	*Increase compared to Ref (%)*
Polyester/fiberglass (Ref)	100.6(9.6)	-	6598(687)	-	190(11)	-
0.01wt% FORZA Graphene	114.9(3.0)	*14.2*	7323(686)	*11.0*	205(10)	*7.7*
0.1wt% FORZA Graphene	124.0(3.9)	*23.2*	7129(441)	*8.1*	200(7)	*4.8*

The strength properties of a matrix material with graphene changes as a function of the graphene concentrations. For polyester the tensile strength increases with increasing concentration for the concentrations measured, while the E-modulus and Maximum flexure seem to go through a maximum value at concentrations below 0.1 wt% graphene. For each different matrix, these properties need to be investigated before concluding on suitable graphene concentrations. For a comparison, with a polylactic acid matrix, no significant strength performance was observed, which could be contributed to low interaction or poor procedures of mixing. However, introducing graphene into different plastic materials has shown to affect other properties than strength, such as increasing electrical and heat conductivity.

3.2 Graphene enhanced epoxy, vinyl esters, and elastomers – properties

Dispersion of graphene is a challenge. FORZA graphene has been dispersed successfully in various matrixes, see e.g. Figure 3-1 where graphene is readily dispersed in poly lactic acid polymer (PLA), however, in order to ensure proper interaction, it may be necessary to functionalize the graphene prior to dispersing it. Dispersion can be done by chemical and physical means or by a mixture of physical and chemical methods. Well dispersed graphene has been obtained in polyesters and different epoxy materials, as well as in in various polymers and coating materials.

Figure 3-1: Graphene dispersed in poly lactic acid polymers (control left) and the graphene version to the right

In addition to altering properties of strength, it has been shown that small concentrations of graphene emerged in nonconductive materials improve the conductivity as well as terahertz absorption. Arthur D. van Rheenen et al. [2] found that introducing as little as 0.1% graphene in epoxy increased the electrical conductivity by a factor 10^8 which was improved even further by increasing the graphene concentration. The implication is that using graphene enhanced materials as coatings have many interesting possible applications due to making insulating materials conductive. The capability of enhancing absorption of microwave and near infrared radiation makes the material interesting in stealth applications.

For elastomers, it has recently been demonstrated that functionalized graphene can be exfoliated and well dispersed into the bulk material. In addition to expected changes in strength of the complex material, the performance on reducing fatigue is expected and are part of ongoing research programs. Proven significant improvement in these properties, may facilitate early commercialization for various applications of low wt% graphene concentrations.

3.3 Direct deposition on carbon fibers and other functional materials

Graphene coating have applications in areas of electronics, mechanical wear reduction, and mechanical strength. Vertical graphene is strongly light absorbing [3]. Vertical graphene coatings can also be incorporated with polymers and existing commercial carbon materials such as carbon fibers for improved strength.

Various materials have been coated with graphene in the FORZA machine. The capability to coat all along the 86 cm width of the plasma tubes makes it possible to have a large area uniform coating up to 6.7 m^2, and could be utilized among others in large scale electronics. Figure 3-2 shows SEM images for growth on a Cr-based Knife blade.

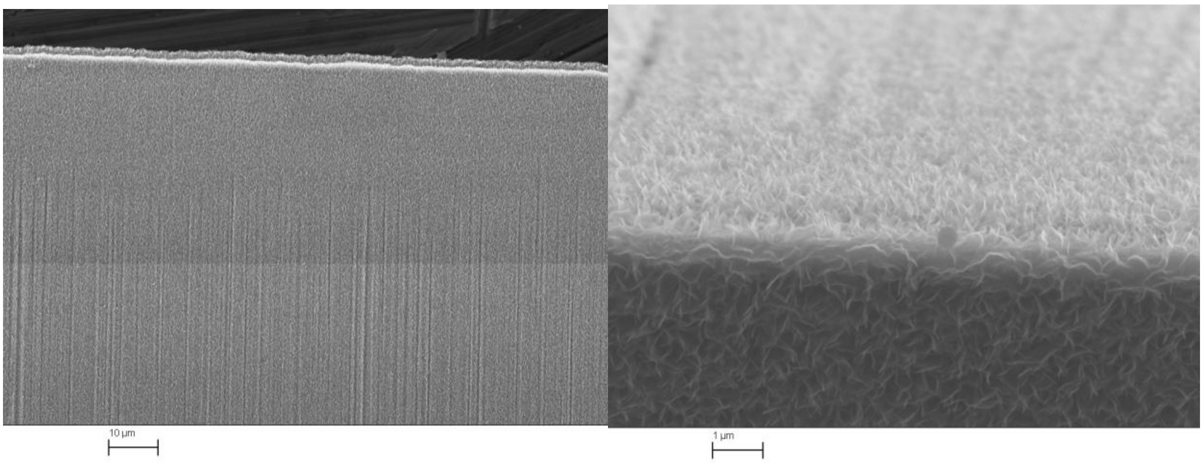

Figure 3-2: SEM images of direct deposition of FORZA graphene on a Cr-based Knife edge. Low resolution side view of the blade to the left and higher resolution from the top to the right

Yao Chi et. al. [4] reported that that the interfacial strength of composites and carbon fibers were immensely improved by 173% by growing graphene nano walls on carbon fibers. So, we have demonstrated that we can grow vertical graphene on carbon fiber bundles (see Figure 3-3), which is topic for our further investigation on improving material strengths.

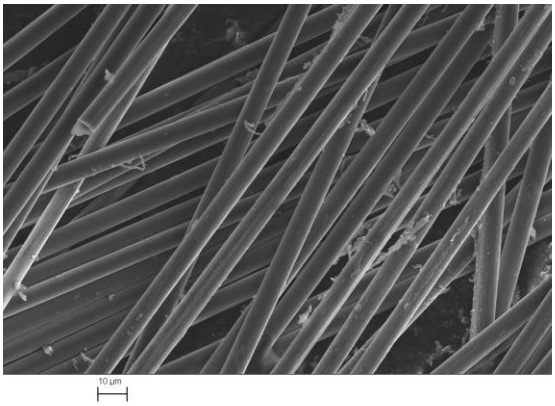

Figure 3-3: SEM images of direct deposition of FORZA graphene on carbon fibres, graphene is seen as the paler material that resides on the darker carbon fibres

3.4 Battery technology

Batteries are critical for the modern military, and the need for charging devices may impair operations, as such time needed for fully charging devices may be a critical factor. Lithium ion battery (LIB) performance includes the aspects of, for example, capacity, battery life and safety. The capacity of a LIB is related to the rate of discharge. LIB experiences increasing capacity drop as discharge rate is increased. Graphene is highly effective in enhancing the capacity as discharge rate increases which means shorter charging time and higher power output of LIB. This is due to high electrical conductivity and better ionic transport kinetics provided by graphene [5]-[6]. A preliminary study was performed at CealTech as shown in Figure 3-4, and demonstrated an improved rate capability of the cathode with graphene. Graphene also helps increasing battery life by mitigating instability of electrode caused by volume expansion and irreversible phase transitions of active material [5]. It is also reported that LIB safety can be improved because graphene can confine the growth of lithium dendrite which is an important cause for shorting the LIB cell leading to fire and even explosion [7].

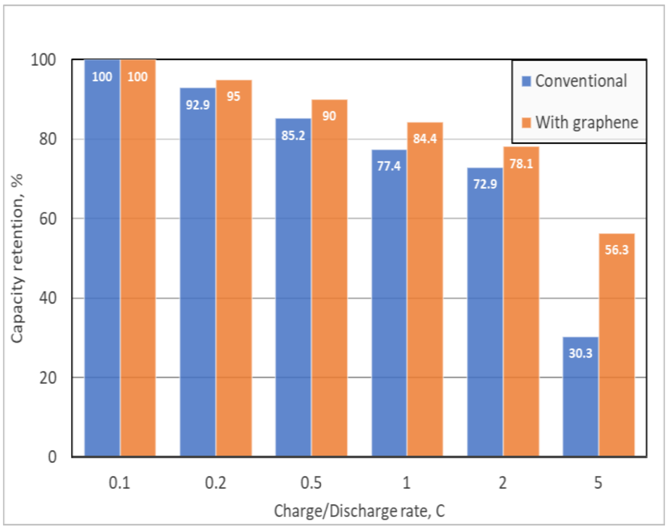

Figure 3-4: Advantage of electrodes incorporated with graphene in fast charging and discharging

4.0 CONCLUSION

We have developed a machine for large scale production of high-quality graphene coating and flakes. The machine is capable of continuous production of graphene flakes as well as coating areas as large as 6.7 m^2. The graphene is found to be of excellent quality.

Dispersion of graphene in a host matrix is essential for successful composites, and CealTech's FORZA graphene has been found to easily disperse in a variety of solvents, polymers, organic compounds, and oils. The FORZA graphene is well suited for composite and energy storage applications. We have explored graphene enhancement of fibre reinforced polymer materials, elastomers, and paints/coatings with regards to improving strength, electrical and thermal conductivity, mechanical and chemical resistance, anti-corrosion, and anti-icing. Vertical graphene is an excellent conductor with a high surface area. We have demonstrated direct deposition of vertical graphene on various materials and in particular on metal foils for use as electrodes for batteries and supercapacitors. The application areas demonstrated are believed to be relevant for military use.

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